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Route to Room-Temperature Superconductivity from a Practical Point of View

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Abstract

To synthesize a new superconductor which has a critical temperature, T_c, exceeding the room temperature, one needs to know what chemical components to start with. This chapter presents analysis of experimental data which allow one to draw a conclusion about components and the structure of a potential room-temperature superconductor. The two essential components of a room-temperature superconductor are large organic molecules (polymers, tissues) and atoms/molecules which are magnetic in the intercalated state. This conclusion is fully based on experimental facts known today, and does not require any assumptions about the mechanism of room-temperature superconductivity. This, however, does not mean that to synthesize a room-temperature superconductor is an easy task.

Never let them persuade you that things are too difficult or impossible.

—Sir Douglas Bader

1 Introduction

The superconducting state is a state of matter: it is a *quantum* state occurring on a macroscopic scale. As any state of matter, superconductivity is not a property of isolated atoms, but is a collective effect determined by the structure of a whole sample. From a classical point of view, the superconducting state is characterized by two distinctive properties: *perfect electrical conductivity* ($\rho = 0$) and *perfect diamagnetism* ($\mathbf{B} = 0$ inside the superconductor, where $\mathbf{B}$ is the magnetic field). After the discovery of the phenomenon of superconductivity in 1911 [1], humans try to derive a good deal of benefit from its peculiar properties. In spite of the fact that superconductivity is a low-temperature phenomenon, the possibility to use a superconductor at room temperature is an old dream.

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It is necessary first to define the expression "a room-temperature superconductor" because some perceive it as a superconductor having a critical temperature $T_c \sim$ 300 K, others as a superconductor functioning at 300 K. There is a huge difference between these two cases. From a technical point of view, superconductors only become useful when they are operated well below their critical temperature—one-half to two-third of that temperature provides a rule of thumb. Therefore, for an engineer, a room-temperature superconductor would be a compound whose resistance disappears somewhere above 450 K. Such a material could actually be used at room temperature for large-scale applications. At the same time, $T_c \sim 350$ K can already be useful for small-scale (low-power) applications. Consequently, unless specified, the expression "a room-temperature superconductor" will further be used to imply a superconductor having a critical temperature $T_c \geq 350$ K.

The invention of the transistor is directly responsible for the way in which silicon technology has so profoundly changed the world in which we live. The availability of a room-temperature superconductor may change our lives even to a greater degree. What technical marvels could we expect to see?

The benefits would range from minor improvements in existing technology to revolutionary upheavals. All devices made from the room-temperature superconductor will be reasonably cheap since its use would not involve cooling cost. Energy savings from many sources would add up to a reduced dependence on conventional power plants. Compact superconducting cables would replace unsightly power lines and revolutionize the electrical power industry. A world with room-temperature superconductivity would unquestionably be a cleaner world and a quieter world. Compact superconducting motors would replace many noisy, polluting engines. Advance transportation systems would lessen our demands on the automobile. Superconducting magnetic energy storage would become commonplace. Computers would be based on compact Josephson junctions. Thanks to the high-frequency, high-sensitivity operation of superconductive electronics, mobile phones would be so compact that could be made in the form of an earring. SQUID (Superconducting QUantum Interference Device) sensors would become ubiquitous in many areas of technology and medicine. Room-temperature superconductivity would undoubtedly trigger a revolution of scientific imagination. The effects of room-temperature superconductivity would be felt throughout society, including children who might well grow up playing with superconducting toys.

In the literature, one can find more than 20 papers reporting evidence of superconductivity near or above room temperature [2]. Most researchers in superconductivity do not accept the validity of these results because they cannot be reproduced by others. The main problem with most of these results is that superconductivity is observed in samples containing many different phases, and the superconducting fraction (if such exists at all) of these samples is usually very small. Thus, superconductivity may exist in these complex materials, but nobody knows what phase is responsible for its occurrence. In a few cases, however, the phase is known but

superconductivity was observed exclusively on the surface. For any substance, the surface conditions differ from those inside the bulk, and the degree of this difference depends on many parameters, and some of them are extrinsic.

Room-temperature superconductivity was already discussed in a book [2]. The main purpose of the book was to show that it is possible to synthesize a room-temperature superconductor. It was concluded that a room-temperature superconductor should consist of large organic molecules (polymers, living tissues) and magnetic atoms/molecules (in the doped state). This outcome is based on **knowledge** of the mechanism of high-temperature superconductivity described in the other book [3]. The mechanism, in its turn, is based on experimental data, mainly, on tunneling measurements obtained in cuprates. However, the **same** conclusion about components and the structure of a room-temperature superconductor can be derived *independently*. This is exactly what we are going to do in this chapter. Thus, to draw a conclusion about components and the structure of a room-temperature superconductor, it is not necessary to make any assumptions about the mechanism of room-temperature superconductivity.

The chapter consists of ten sections and is organized as follows. In the following section, we shall briefly discuss guidelines for materials that superconduct at high temperatures, presented by Geballe in 1993. The third section describes the physical properties of known superconductors. It turns out that all superconductors can be classified into three groups according to their structural and magnetic properties. From the analysis of superconducting properties, one can easily infer that a potential room-temperature superconductor can only belong to one of these three groups, and not to the other two. Knowledge of the common physical properties of this group, which are analyzed in the fourth section, gives an opportunity to know what physical properties should we expect from a room-temperature superconductor. In the fifth section, we shall discuss the most important requirements for materials that superconduct at high temperatures. The principles of superconductivity are briefly discussed in the sixth section. Bearing in mind the information presented in the first six sections, an approach to room-temperature superconductivity is proposed in the seventh section. The presence of bipolarons (bisolitons) in some non-superconducting polymers and large organic molecules at room temperature is discussed in the following section. Components and the structure of a promising room-temperature superconductor are considered in the ninth section. The chapter ends with conclusions.

2   Geballe's guidelines

In 1992, a diverse group of researchers gathered at a two-day workshop in Bodega Bay (California). They considered the issue of making much higher temperature superconductors. T. H. Geballe, who attended this workshop, summarized some guidelines in a two-page paper published in *Science* [4], that emerged from the

discussions:

- Materials should be multicomponent structures with more than two sites per unit cell, where one or more sites not involved in the conduction band can be used to introduce itinerant charge carriers.

- Compositions should be near the metal-insulator Mott transition.

- On the insulating side of the Mott transition, the localized states should have spin-1/2 ground states and antiferromagnetic ordering of the parent compound.

- The conduction band should be formed from antibonding tight-binding states that have a high degree of cation-anion hybridization near the Fermi level. There should be no extended metal-metal bonds.

- Structural features that are desirable include two-dimensional extended sheets or clusters with controllable linkage, or both.

These hints are mainly based on knowledge of the physical properties of cuprates. In a sense, one of our tasks in this chapter is to extend these guidelines.

3   Three groups of superconductors

The task to synthesize a room-temperature superconductor is a materials-physics problem. Therefore, it is worthwhile to review superconducting compounds. Classify all superconducting materials into three groups. The groups consist of superconductors which are:
1) **three-dimensional and non-magnetic,**
2) **low-dimensional and non-magnetic,** and
3) **low-dimensional and magnetic.**
Recently, it was shown that the mechanisms of superconductivity in compounds of these three groups are different [2, 3]. However, this issue is not important in the context of this chapter. As was mentioned in the Introduction, in order to draw a conclusion about components and the structure of a room-temperature superconductor, we shall not try to understand possible mechanisms of room-temperature superconductivity. Let us briefly review a few superconductors from these three groups (for more information, see [2]).

3.1   First group of superconducting materials

The first group of superconductors incorporates non-magnetic elemental superconductors and some of their alloys. The superconducting state in these materials is well described by the BCS theory of superconductivity [5]. Thus, this group of

superconductors includes all classical, conventional superconductors. The critical temperature of these superconductors **does not** exceed 10 K. Most of them are type-I superconductors. As a consequence, superconductors from this group are not suitable for applications because of their low transitional temperature and low critical field.

Ironically, many superconductors, discovered mainly before 1986, were assigned to this group by mistake. In fact, they belong to either the second or third group of superconductors. For example, the so-called A-15 superconductors, during a long period of time, were considered as conventional; in reality, they belong to the second group. The so-called Chevrel phases were first assigned also to the first group; however, superconductivity in Chevrel phases is of unconventional type, and they are representatives of the third group of superconductors.

Some elements which superconduct under high pressure belongs either to the third or the second group of superconductors. Under high pressure, their crystal structure becomes low-dimensional, often containing simultaneously two- and one-dimensional substructures. In addition, some of them are magnetic. For example, under extremely high pressure, iron exhibits superconductivity which is of unconventional type. Thus, the number of superconductors in the first group is in fact very small, and they are not suitable for applications.

3.2   Second group of superconducting materials

The second group of superconductors incorporates low-dimensional and non-magnetic compounds, such as A-15 superconductors, the metal oxide $Ba_{1-x}K_xBiO_3$, the magnesium diboride MgB_2 and a large number of other binary compounds. The superconducting state in these materials is characterized by the presence of two interacting superconducting subsystems. One of them is low-dimensional and exhibits genuine superconductivity of unconventional type, while superconductivity in the second subsystem which is three-dimensional is often induced by the first one and of the BCS type. So, superconductivity in this group of materials can be called half-conventional (or alternatively, half-unconventional). The critical temperature of these superconductors is **limited** by ~ 40 K and, in some of them, T_c can be tuned. All of them are type-II superconductors with an upper critical magnetic field usually exceeding 10 T. Therefore, many superconductors from this group are suitable for different types of practical applications.

• Intermetallic compounds of transition metals of niobium (Nb) and vanadium (V) such as Nb_3B and V_3B, where B is one of the nontransitional metals, have the structure of beta-tungsten (β-W) designated in crystallography by the symbol A-15. As a consequence, superconductors having the structure A_3B (A = Nb, V, Ta, Zr and B = Sn, Ge, Al, Ga, Si) are called the A-15 superconductors. Nb_3Ge has the highest critical temperature, $T_c = 23.2$ K. The critical temperature of A-15 superconductors is very sensitive to changes in the 3:1 stoichiometry. In the crystal structure of the binary A_3B compounds, the atoms B form a body-centered cubic

sublattice, while the atoms A are situated on the faces of the cube forming three sets of non-interacting orthogonal one-dimensional chains.

• Superconductivity in the metal oxide $BaPb_{1-x}Bi_xO_3$ was discovered in 1975, which has a maximum $T_c \simeq 13.7$ K at $x = 0.25$. Other members of this family are $BaPb_{0.75}Sb_{0.25}O_3$ ($T_c = 0.3$ K) and $Ba_{1-x}K_xBiO_3$ (BKBO). The metal oxide BKBO is an exceptionally interesting material and the first oxide superconductor without copper with a critical temperature above that of all the A-15 compounds. Its critical temperature is $T_c \simeq 32$ K at $x = 0.4$. At the moment of writing, BKBO still exhibits the highest T_c known for an oxide other than the cuprates. Superconducting BKBO with low potassium content exhibits a charge-density-wave ordering. The density of charge carriers in BKBO is very low. Various evidence suggests that the electron-phonon coupling is responsible for superconductivity in BKBO. A two-band model applied to BKBO accounts very well for all the available data on BKBO. Acoustic measurements performed in BKBO show that many physical properties of BKBO are quite similar to those of the A-15 superconductors.

• In January 2001, magnesium diboride MgB_2 was found to superconduct at T_c = 39 K. At the moment of writing, the intermetallic MgB_2 has the highest critical temperature at ambient pressure among all superconductors with the exception of superconducting cuprates. The crystal structure of MgB_2 is composed of layers of boron and magnesium, alternating along the c axis. Each boron layer has a hexagonal lattice similar to that of graphite. The magnesium atoms are arranged between the boron layers in the centers of the hexagons. Superconductivity in MgB_2 occurs in the boron layers. The electron-phonon interaction seems to be responsible for the occurrence of superconductivity in MgB_2. The density of states in MgB_2 is small. MgB_2 has a very low normal-state resistance: at 42 K the resistivity of MgB_2 is more than 20 times smaller than that of Nb_3Ge in its normal state. MgB_2 has two energy gaps, $\Delta_L/\Delta_s \simeq 2.7$. Seemingly, both the energy gaps have s-wave symmetries: the larger gap is highly anisotropic, while the smaller one is either isotropic or slightly anisotropic. The larger energy gap Δ_L occurs in the σ-orbital band, while Δ_s in the π-orbital band.

• There are a large number of binary superconductors. Non-magnetic binary compounds exhibiting high values of T_c and H_{c2} belong to the second group of superconductors, such as *nitrides*, *carbides* and *laves phases*. Nitrides and carbides are also known as B1 superconductors. Metallic AB_2 compounds that superconduct are called the laves phases. Semiconductors, e.g. GeTe and SnTe, also belongs to the second group of superconductors.

3.3   Third group of superconducting materials

The third group of superconductors is the largest and incorporates superconductors which are low-dimensional and magnetic, or at least, these compounds have strong magnetic correlations. This is basically the group of unconventional superconductors. Superconductors with the highest critical temperature belong to this

group—cuprates show $T_{c,max} \simeq 135$ K.

In the majority of unconventional superconductors, the magnetic correlations favor an antiferromagnetic ordering. In contrast to antiferromagnetic superconductors, ferromagnetic ones usually have a low critical temperature. The density of charge carriers in these superconductors is very low. All unconventional superconductors are of type-II. They have a very large upper critical magnetic field. As a consequence, many superconductors from this group are used for practical applications. In this subsection we shall briefly discuss the following compounds from the third group of superconductors: Chevrel phases, cuprates, charge transfer organics, fullerides, graphite intercalation compounds, non-organic polymers, carbon nanotubes, heavy fermions, nickel borocarbides, the strontium ruthenate, ruthenocuprates, $MgCNi_3$, $Cd_2Re_2O_7$, $Na_xCoO_2 \cdot yH_2O$, hydrides and deuterides. We start with the so-called Chevrel phases.

3.3.1 Chevrel phases

In 1971, Chevrel and co-workers discovered a new class of ternary molybdenum sulfides, having the general chemical formula $M_xMo_6S_8$, where M stands for a large number of metals and rare earths (nearly 40), and $x = 1$ or 2. The Chevrel phases with S substituted by Se or Te also display superconductivity. Before the discovery of high-T_c superconductivity in cuprates, the A-15 superconductors had the highest values of T_c, but the Chevrel phases were the record holders in exhibiting the highest values of upper critical magnetic field H_{c2}. $PbMo_6S_8$ has the highest critical temperature, $T_c \simeq 15$ K, and upper critical magnetic field, $H_{c2} \simeq 60$ T. Superconductivity in the Chevrel phases coexists with antiferromagnetism of the rare earth elements. For example, a long-range antiferromagnetic order of the rare earth elements RE = Gd, Tb, Dy and Er in $(RE)Mo_6X_8$, setting in respectively at $T_N = 0.84$, 0.9, 0.4 and 0.15 K, coexists with superconductivity occurring at $T_c = 1.4$, 1.65, 2.1 and 1.85 K, respectively, where T_N is the Néel temperature. Superconductivity in the Chevrel phases is primarily associated with the mobile $4d$-shell electrons of Mo, while the magnetic order involves the localized $4f$-shell electrons of the rare earth atoms which occupy regular positions throughout the lattice.

The crystal structure of Chevrel phases is quite interesting. These compounds crystallize in a hexagonal-rhombohedral structure. The building blocks of the Chevrel-phase crystal structure are the M elements and Mo_6X_8 molecular clusters. Each Mo_6X_8 is a slightly deformed cube with X atoms at the corners, and Mo atoms at the face centers. The electronic and superconducting properties of these compounds depend mainly on the Mo_6X_8 group, with the M ion having very little effect.

3.3.2   Cuprates

A compound is said to belong to the family of copper oxides (cuprates) if it has the CuO_2 planes. Cuprates that superconduct are also called high-T_c superconductors. The first high-T_c superconductor was discovered in 1986 by Bednorz and Müller at IBM Zurich Research Laboratory. The parent compounds of superconducting cuprates are antiferromagnetic Mott insulators. The cuprates and $Na_x CoO_2 \cdot yH_2O$ (see below) are the only Mott insulators known to superconduct. $HgBa_2 Ca_2 Cu_3 O_{10}$ has the highest critical temperature at ambient pressure, $T_c = 135$ K. The crystal structure of cuprates is of a perovskite type, and it is highly anisotropic. Superconductivity in cuprates occur in CuO_2 planes. The CuO_2 layers in the cuprates are always separated by layers of other atoms such as Bi, O, Y, Ba, La etc., which provide the charge carriers into the CuO_2 planes. The ground state of CuO_2 planes is antiferromagnetic. The $T_c(p)$ dependence has a nearly bell-like shape, where p is the hole (electron) concentration in the copper oxides planes. In spite of the fact that the structure of cuprates is two-dimensional, the in-plane transport properties are quasi-one-dimensional. One compound $YBa_2 Cu_3 O_{6+x}$ has one-dimensional CuO chains. The majority of superconducting cuprates are hole-doped. The number of electron-doped cuprates is very limited, e.g. $Nd_{2-x} Ce_x CuO_4$ and $Pr_{2-x} Ce_x CuO_4$.

3.3.3   Charge transfer organics

Organic compounds are usually insulators. It turns out that some of them superconduct at low temperatures. The first organic superconductor was discovered in 1979 by Jerome and Bechgaard: the compound $(TMTSF)_2 PF_6$ was found to superconduct below $T_c = 0.9$ K under a pressure of 12 kbar. TMTSF denotes tetramethyltetraselenafulvalene, and PF_6 is the hexafluorophosphate. However, the ten years following this discovery saw a remarkable increase in T_c. In 1990, an organic superconductor with $T_c \approx 12$ K was synthesized. In only 10 years, T_c increased over a factor 10! All organic superconductors are layered; therefore, basically they are two-dimensional. However, the electron transport in some of them is quasi-one-dimensional.

Figure 1 shows several organic molecules that form superconductors. In general, they are flat, planar molecules. Among other elements, these molecules contain sulfur or selenium atoms. In a crystal, these organic molecules are arranged in stacks. The chains of other atoms or molecules (PF_6, ClO_4 etc.) are aligned in these crystals parallel to the stacks. As an example, the crystal structure of the first organic superconductor $(TMTSF)_2 PF_6$, a representative of the *Bechgaard salts*, is schematically shown in Fig. 2. The planar TMTSF molecules form stacks along which the electrons are most conducting (the a axis). The chains of PF_6 lie between the stacks, aligned parallel to them. Two molecules TMTSF donate one electron to an anion PF_6. The separation of charge creates electrons and holes that can become delocalized to render the compound conducting and, at low temperatures, superconducting (under pressure).
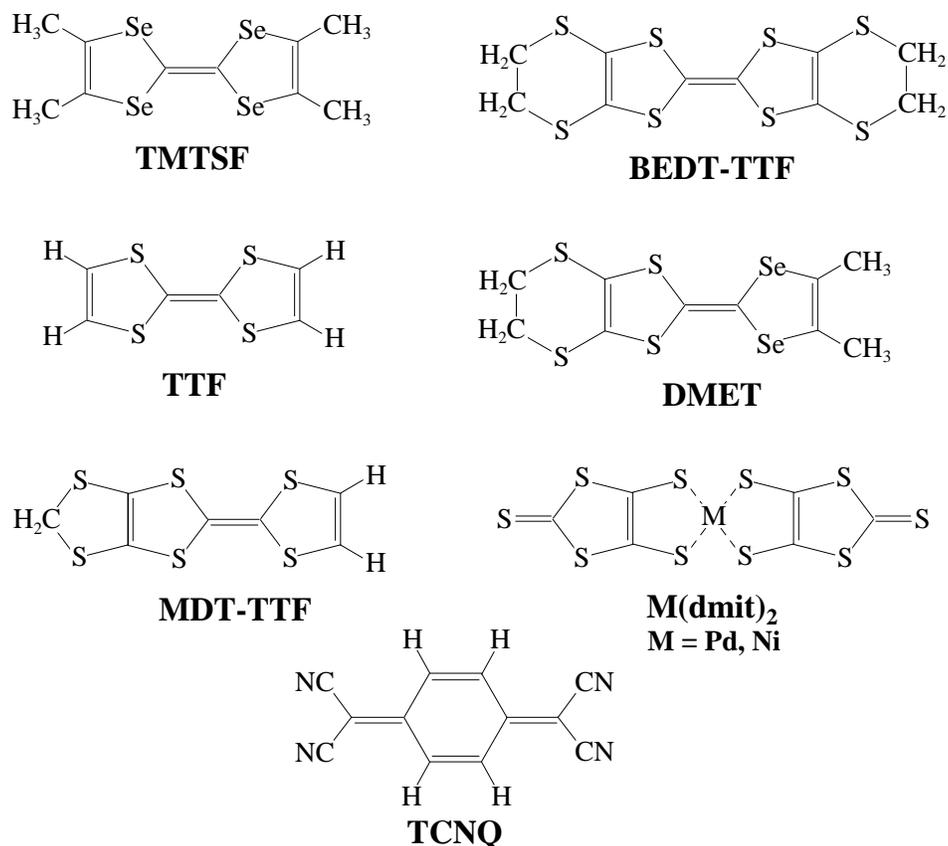
Figure 1: Structure of organic molecules that form superconductors. Abbreviations of their names are shown below each molecule.

After 1979, several more organic superconductors of similar structure were discovered. In all cases, some anion X^- is needed to affect charge balance in order to obtain metallic properties and, at low temperature, superconductivity. So, the anions are mainly charge-compensating spacers; the conductivity is in the organic molecules. There are six different classes of organic superconductors. Two of them are the most studied—the Bechgaard salts $(TMTSF)_2X$ and the organic salts $(BEDT\text{-}TTF)_2X$ based on the compound BEDT-TTF shown in Fig. 1. BEDT-TTF denotes bis-ethylenedithio-tetrathiafulvalene. The members of the (BEDT-TTF)$_2$X family exhibit the highest values of T_c, and have a rich variety of crystalline structures. In contrast to the Bechgaard salts which exhibit quasi-one-dimensional electron transport, the electronic structure of the BEDT-TTF family is of two-dimensional nature. The highest values of T_c are observed in the (BEDT-TTF)$_2$X salts with the anions $X = Cu(NCS)_2$; $Cu[N(CN)_2]Br$ and $Cu[N(CN)_2]Cl$. Their critical temperatures are respectively $T_c = 10.4$, 11.6 and 12.8 K. The first two com-

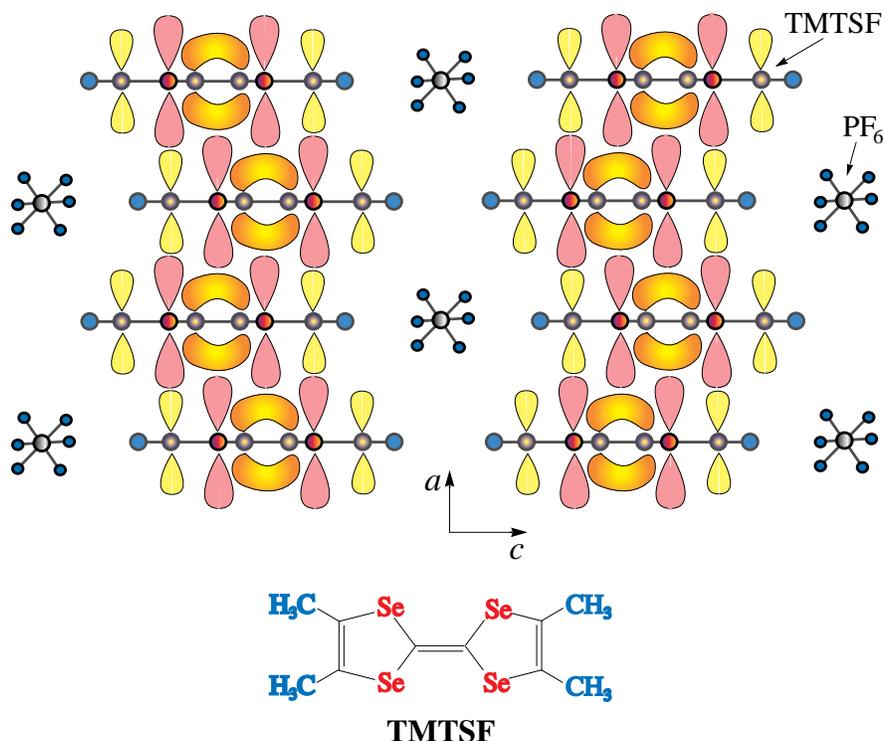Figure 2: A side view of the crystal structure of the Bechgaard salt $(TMTSF)_2PF_6$. Each TMTSF molecule is shown with the electron orbitals (the hydrogen atoms are not shown). The chemical structure of the TMTSF molecule is depicted at the bottom. The organic salt $(TMTSF)_2PF_6$ is the most conductive along the TMTSF stacks (along the a axis).

pounds superconduct at ambient pressure, while the last one with $Cu[N(CN)_2]Cl$ becomes superconducting under a pressure of 0.3 kbar.

Depending on pressure, organic superconductors exhibit a long-range antiferromagnetic ordering. If, in the phase diagram of the Bechgaard salts, the superconducting phase evolves out of the antiferromagnetic phase, in the organic salt k-$(BEDT$-$TTF)_2Cu[N(CN)_2]Br$, these two phases overlap. This suggests that antiferromagnetic fluctuations—short-lived excitations of the hole-spin arrangements— are important in the mechanism of unconventional superconductivity in organic salts.

The quasi-two-dimensional organic conductor λ-$(BETS)_2FeCl_4$, superconductivity is induced by a very strong magnetic field, $18 \leq H \leq 41$ T [2]. The dependence $T_c(H)$ has a bell-like shape with a maximum $T_c \simeq 4.2$ K near 33 T. At zero field, this organic compound is an antiferromagnetic insulator below 8.5 K. The other two-dimensional compound, α-$(BEDT$-$TTF)_2KHg(NCS)_4$, at low magnetic fields is

a charge-density-wave insulator. Thus, in these organic salts, the magnetic and electronic degrees of freedom are coupled. Furthermore, the fact that the electronic and magnetic properties of organic superconductors strongly depend on pressure indicates that their electronic, magnetic and crystal structures are strongly coupled.

3.3.4   Fullerides

Historically, any allotrope based on the element carbon has been classed as organic, but a new carbon allotrope stretches that definition. The pure element carbon forms not only graphite and diamond but a soccer-ball shaped molecule containing 60 atoms called buckminster-fullerene or buckyball. There are also lower and higher molecular weight variations such as C_{20}, C_{28}, C_{70}, C_{72}, C_{100} and so forth, which share many of the same properties. The word "fullerenes" is now used to denote all these molecules and other closed-cage molecules consisting of only carbon atoms.

C$_{60}$ was discovered in 1985. In 1991 it was found that intercalation of alkali-metal atoms in solid C_{60} leads to metallic behavior. The alkali-doped fullerenes are called fullerides. Shortly afterwards, also in 1991, it was discovered that some of these alkali-doped C_{60} compounds are superconducting. In fullerides, the maximum critical temperature of 33 K is observed at ambient pressure in $RbCs_2C_{60}$, and T_c = 40 K in Cs_3C_{60} under a pressure of 12 kbar. Unfortunately, the fullerides are extremely unstable in air, burning spontaneously, so they must be prepared and kept in an inert atmosphere. The fullerides are magnetic due to spins of alkali atoms, which are ordered antiferromagnetically at low temperatures. The fullerides are electron-doped superconductors, not hole-doped as cuprates and organic salts. The values of H_{c1} in the fullerides are very small, $\sim$ 100–200 Oe, whilst those of H_{c2} are sufficiently large for electron-doped superconductors, $\sim$ 30–50 T.

3.3.5   Graphite intercalation compounds

The first observation of superconductivity in doped graphite goes back to 1965, when superconductivity was observed in the potassium graphite intercalation compound C_8K having a critical temperature of 0.55 K. Later, superconductivity was observed in other graphite intercalation compounds (GICs). A single layer of three-dimensional graphite is defined as a *graphene* layer. In GICs, the graphene layers are separated by the layers of intercalant atoms. According to the preparation method, the superconducting GICs can be divided into two subgroups: the stage 1 and stage 2 GICs. The stage 2 GICs are synthesized in two stages. The structures of the stage 1 and 2 GICs are different along the c axis. In the stage 1 GICs, the adjacent intercalant layers are separated from one another by *one* graphene layer, while in the stage 2 GICs, the neighboring intercalant layers are separated by *two* graphene layers. The stage 1 GICs consist of the binary C_8M, ternary C_4MHg and $C_4MTl_{1.5}$ compounds, and the stage 2 GICs are represented by the ternary C_8MHg and $C_8MTl_{1.5}$, where M = K, Rb and Cs. In the superconducting GICs, as well as

in the fullerides, the charge carriers are electrons, not holes.

For binary C_8M compounds, the highest critical temperatures reported for M = K, Rb and Cs are 0.55, 0.15 and 0.135 K, respectively. In the alkali metal amalgam GICs C_8KHg and C_8RbHg, the critical temperatures are 1.93 and 1.44 K, respectively. In the potassium thallium GICs $C_4KTl_{1.5}$ and $C_8KTl_{1.5}$, respectively T_c = 2.7 and 1.3 K. With the potassium thallium GICs excluded, the critical temperature of the stage 2 GICs is in general higher than that of the stage 1 GICs. Under pressure, the sodium graphite intercalation compound C_2Na superconducts below $T_c \sim 5$ K. All the GICs are two-dimensional. In $C_4KTl_{1.5}$ which has the highest T_c at ambient pressure (= 2.7 K), $H_{c2,\perp} \simeq 3$ T.

At the moment of writing, superconductivity in the isostructural graphite intercalation compounds C_6Yb and C_6Ca, with transition temperatures of 6.5 K and 11.5 K, respectively, was discovered [6].

3.3.6 $(SN)_x$ polymer

$(SN)_x$ is a chain-like inorganic polymer in which sulphur and nitrogen atoms alternate along the chain. When doped with bromine, it becomes superconducting below $T_c = 0.3$ K. Its unit cell contains two parallel spirals of $(SN)_x$ twisted in the opposite directions. The Br_3^- and Br_5^- clusters are situated between the $(SN)_x$ spirals. Superconductivity in $(SN)_x$ was discovered in 1975. It is the first superconductor found among quasi-one-dimensional conductors and, moreover, the first that does not contain metallic elements. The single crystals have a *dc* electrical conductivity of about 1.7×10^5 $\Omega^{-1} \, m^{-1}$ along the chains, and the anisotropy is of the order of 10^3. A remarkable property of $(SN)_x$ is that it does not undergo a metal-insulator (Peierls) transition at low temperatures but turns instead into a superconductor below 0.3 K.

3.3.7   Carbon nanotubes

In addition to ball-like fullerenes, it is possible to synthesize tubular fullerenes. By rolling a graphene sheet into a cylinder and capping each end of the cylinder with a half of a fullerene molecule, a fullerene-derived tubule, one atomic layer, is formed. Depending on the wrapping angle, one can have three types of the nanotubes: zigzag, armchair and chiral. The armchair nanotubes are usually metallic, while the zigzag ones are semiconducting. The carbon nanotubes and fullerenes have a number of common features and also many differences. Carbon nanotubes can be viewed as giant conjugated molecules with a conjugated length corresponding to the whole length of the tube. The nanotubes have an impressive list of attributes. They can behave like metals or semiconductors, can conduct electricity better than copper, can transmit heat better than diamond. They rank among the strongest materials known, and they can superconduct at low temperatures.

Carbon nanotubes were found by Iijima in 1991 in Japan. In fact, they were multi-walled carbon nanotubes consisting of several concentric single-walled nanotubes nested inside each other, like a Russian doll. Two years later, single-walled nanotubes were seen for the first time. In 1999, proximity-induce superconductivity below 1 K was observed in single-walled carbon nanotubes, followed by the observation of genuine superconductivity with $T_c = 0.55$ K. In the latter case, the diameter of single-walled nanotubes was of the order of 14 Å. Soon afterwards, superconductivity below $T_c \simeq 15$ K was seen in single-walled carbon nanotubes with a diameter of 4.2 Å.

3.3.8   Heavy-fermion systems

This family of superconductors includes superconducting compounds which consist of one magnetic ion with $4f$ or $5f$ electrons (usually Ce or U) and other constituent or constituents being s, p, or d electron metals. The principal feature of these materials is reflected in their name: below a certain coherence temperature (~ 20–100 K), the effective mass of charge carriers in these compounds become gigantic, up to several hundred times greater than that of a free electron. A large number of heavy fermions superconduct exclusively under pressure. The T_c values of superconducting heavy fermions are in general very low; however, the family of these intermetallic compounds is one of the best examples of highly correlated condensed matter systems. The crystal structure of these compounds does not have a common pattern, but varies from case to case. For example, the crystal structure of the first discovered superconducting heavy fermions—$CeCu_2Si_2$, UBe_{13} and UPt_3—is tetragonal, cubic and hexagonal, respectively.

The first heavy fermion, $CeCu_2Si_2$, was discovered in 1979 by Steglich and co-workers, and some time passed before the heavy-fermion phenomenon was confirmed by the discovery of UBe_{13} and then UPt_3, with critical temperatures of $T_c = 0.65$, 0.9 and 0.5 K, respectively. Since then many new heavy-fermion systems that superconduct at low temperatures have been found.

Probably, the most interesting characteristic of superconducting heavy fermi-on materials is the interplay between superconductivity and magnetism. The magnetic ions are responsible for the magnetic properties of heavy fermions. For example, in the heavy fermions UPt_3, URu_2Si_2, UCu_5 and $CeRhIn_5$, magnetic correlations lead to an itinerant spin-density-wave order, while, in UPd_2Al_3 and $CeCu_2Si_2$, to a localized antiferromagnetic order. In the latter two heavy fermions, the antiferromagnetic order appears first, followed by the onset of superconductivity. In these compounds, as well as in other superconducting heavy fermions with long-range antiferromagnetic order, the Néel temperature is about $T_N \sim 10T_c$. For instance, in $CeRh_{0.5}Ir_{0.5}In_5$ and $CeRhIn_5$, the bulk superconductivity coexists *microscopically* with small-moment magnetism ($\leq 0.1\mu_B$). In the heavy fermion $CeIrIn_5$, the onset of a small magnetic field (~ 0.4 Gauss) sets in exactly at T_c.

Recently, superconductivity was discovered in $PuCoGa_5$, the first superconduct-

ing heavy fermion based on plutonium. What is even more interesting is that the superconductivity survives up to an astonishingly high temperature of 18 K.

It was a surprise when in 2000 the coexistence of superconductivity and ferromagnetism was discovered in an alloy of uranium and germanium, UGe_2. At ambient pressure, UGe_2 is known as a metallic ferromagnet with a Curie temperature of T_C = 53 K. However, as increasing pressure is applied to the ferromagnet, T_C falls monotonically, and appears to vanish at a critical pressure of $P_c \simeq$ 16–17 kbars. In a narrow range of pressure below P_c and thus *within* the ferromagnetic state, the superconducting phase appears in the millikelvin temperature range below the critical temperature. Soon after the discovery of superconductivity in itinerant ferromagnet UGe_2, two new itinerant ferromagnetic superconductors were discovered—zirconium zinc $ZrZn_2$ and uranium rhodium germanium URhGe.

3.3.9   Nickel borocarbides

The nickel borocarbide class of superconductors has the general formula RNi_2B_2C, where R is a rare earth being either magnetic (Tm, Er, Ho, or Dy) or nonmagnetic (Lu and Y). In the case when R = Pr, Nd, Sm, Gd or Tb in RNi_2B_2C, the Ni borocarbides are not superconducting at low temperatures but antiferromagnetic. In the Ni borocarbides with a magnetic rare earth, superconductivity coexists at low temperatures with a long-range antiferromagnetic order. Interestingly, while in the superconducting heavy fermions with a long-range antiferromagnetic order $T_N \sim 10T_c$, in some Ni borocarbides it is just the opposite, $T_c \sim 10T_N$. Thus, antiferromagnetism appears deeply in the superconducting state.

Superconductivity in the Ni borocarbides was discovered in 1994 by Eisaki and co-workers. Transition temperatures in these quaternary intermetallic compounds can be as high as 17 K. The Ni borocarbides have a layered-tetragonal structure alternating RC sheets and Ni_2B_2 layers. As a consequence, the superconducting properties of the Ni borocarbides are also anisotropic. The layered borocarbides DyB_2C and HoB_2C without Ni also superconduct, with T_c = 8.5 and 7.1 K, respectively. Other related compounds, such as the Ni boronitride $La_3Ni_2B_2N_3$, are also found to superconduct.

3.3.10   Strontium ruthenate

Nearly 40 years ago it was found that $SrRuO_3$ is a ferromagnetic metal with a Curie temperature of 160 K. In its cousin, Sr_2RuO_4, the superconducting state with $T_c \approx$ 1.5 K was discovered in 1994 by Maeno and his collaborators. The crystal structure of Sr_2RuO_4 is layered perovskite, and almost isostructural to the high-T_c parent compound La_2CuO_4, in which the CuO_2 layers are substituted by the RuO_2 ones. Recently, bilayer and trilayer strontium ruthenates have been synthesized: $Sr_3Ru_2O_7$ is an enhanced paramagnetic metal, and $Sr_4Ru_3O_{10}$ is ferromagnetic with a Curie temperature of 105 K.

3.3.11   Ruthenocuprates

Ruthenocuprates are in a sense a hybrid of superconducting cuprates and the strontium ruthenate. As a consequence, they have a number of common features with the cuprates, but also many differences. Basically, there are two ruthenocuprates that superconduct at low temperatures. The general formulas of these ruthenocuprates are $RuSr_2RCu_2O_8$ and $RuSr_2R_2Cu_2O_{10}$ with R = Gd, Eu and Y. The second ruthenocuprate was discovered first in 1997. The crystal structure of $RuSr_2RCu_2O_8$ is similar to that of $YBa_2Cu_3O_7$ except for the replacement of one-dimensional CuO chains by two-dimensional RuO_2 layers. It is assumed that the RuO_2 layers act as charge reservoirs for the CuO_2 layers. The principal feature of the ruthenocuprates is that they are magnetically ordered below $T_m \sim 130$ K, and become superconducting at $T_c \sim 40$ K. For $RuSr_2RCu_2O_8$, $T_m = 130$–150 K and $T_c = 30$–45 K, while for $RuSr_2R_2Cu_2O_{10}$, $T_m = 90$–180 K and $T_c = 30$–40 K. It is believed that the magnetic order arises from ordering of Ru ions in the RuO_2 layers, while the transport occurs in the CuO_2 layers. Superconductivity and the magnetic order are found to be homogeneous. There is a consensus that in the ruthenocuprate, there is a small ferromagnetic component; however, there is no agreement on its origin. It may originate not only from the Ru moments but also, for example, from the Gd spins.

3.3.12 $MgCNi_3$

Superconductivity in $MgCNi_3$ was discovered in 2001 by Cava and co-workers, a few months later than that in MgB_2. The crystal structure of $MgCNi_3$ is cubic-perovskite, and similar to that of BKBO. The perovskite $MgCNi_3$ is special in that it is neither an oxide nor does it contain any copper. Since Ni is ferromagnetic, the discovery of superconductivity in $MgCNi_3$ was surprising. The critical temperature is near 8 K. $MgCNi_3$ is metallic, and the charge carriers are electrons which are derived predominantly from Ni. Structural studies of $MgCNi_3$ reveal structural inhomogeneity. Apparently, the perovskite cubic structure of $MgCNi_3$ is modulated locally by the variable stoichiometry on the C sites.

3.3.13 $Cd_2Re_2O_7$

Although $Cd_2Re_2O_7$ was synthesized in 1965, its physical properties remained almost unstudied. Unexpectedly, superconductivity in $Cd_2Re_2O_7$ was discovered in the second half of 2001 by Sakai and co-workers. The critical temperature of $Cd_2Re_2O_7$ is low, $T_c = 1$–1.5 K. This compound is the first superconductor found among the large family of pyrochlore oxides with the formula $A_2B_2O_7$, where A is either a rare earth or a late transition metal, and B is a transition metal. In this structure, the A and B cations are 4- and 6-coordinated by oxygen anions. The A-O_4 tetrahedra are connected as a pyrochlore lattice with straight A-O-A bonds,

while B-O_6 octahedra form a pyrochlore lattice with the bent B-O-B bonds with an angle of 110–140°. Assuming that electronic structure in $Cd_2Re_2O_7$ as formally Cd^{2+} $4d^{10}$ and Re^{5+} $4f^{14}5d^2$, the electronic and magnetic properties are primarily dominated by the Re $5d$ electrons.

Oxide superconductors with non-perovskite structure are rare. Previous studies indicate that the pyrochlores, like the spinels, are geometrically frustrated. The effect of geometric frustration on the physical properties of spinel materials is drastic, resulting in, for example, heavy-fermion behavior in LiV_2O_4. Another spinel compound $LiTi_2O_4$ is a superconductor below $T_c = 13.7$ K. Indeed, x-ray diffraction studies performed under high pressure showed that superconductivity in $Cd_2Re_2O_7$ is detected only for the phases with a structural distortion. It was suggested that the charge fluctuations of Re ions play a crucial role in determining the electronic properties of $Cd_2Re_2O_7$.

3.3.14 $Na_xCoO_2 \cdot yH_2O$

One of the newest superconductors is the layered cobalt oxyhydrate $Na_xCoO_2 \cdot yH_2O$ ($\frac{1}{4} < x < \frac{1}{3}$ and $y = 1.3$–1.4). The structure of the parent compound Na_xCoO_2 consists of alternating layers of CoO_2 and Na. In the hydrated Na_xCoO_2, the water molecules form additional layers, intercalating all CoO_2 and Na layers. After the hydration of Na_xCoO_2, the c-axis lattice parameter increases from 11.16 Å to 19.5 Å. Thus, the elementary cell of $Na_xCoO_2 \cdot yH_2O$ consists of three layers of CoO_2, two layer of Na^+ ions and four layers of H_2O. Within each CoO_2 layer, the Co ions occupy the sites of a triangular lattice. The 1 - x fraction of Co ions is in the low spin $S = \frac{1}{2}$ Co^{4+} state, while the x fraction is in the $S = 0$ Co^{3+} state. In the triangular lattice, the spins of Co^{4+} ions are ordered antiferromagnetically.

Superconductivity in $Na_xCoO_2 \cdot yH_2O$ occurs in the CoO_2 layers. The superconducting phase as a function of x has a bell-like shape, situated between 0.25 and 0.33 with a maximum $T_c \simeq 4.5$ K near $x = 0.3$. $Na_xCoO_2 \cdot yH_2O$ is the first superconductor containing water (ice). All experimental facts indicate that the presence of water is crucial to superconductivity.

3.3.15   Hydrides and deuterides

In addition to the nitrides and carbides from the second group of superconductors, another class of superconducting compounds that also have the NaCl structure includes hydrides and deuterides (i.e. compounds containing hydrogen or deuterium). However, in contrast to the nitrides and carbides, superconducting hydrides and deuterides are magnetic. In the seventies it was discovered that some metals and alloys, not being superconducting in pure form, become relatively good superconductors when they form alloys or compounds with hydrogen or deuterium. These metals include the transition elements palladium (Pd) and thorium (Th) that have unoccupied $4d$- and $5f$-electron shells, respectively.

In 1972, Skoskewitz discovered that the transition element Pd which has a small magnetic moment normally preventing the pairing of electrons, joins hydrogen and forms the PdH compound that superconducts at $T_c = 9$ K. Later on, it was found that by doping such a system with noble metals the critical temperature increases up to 17 K. Interestingly, the palladium-deuterium compound also superconducts, and its critical temperature equal to 11 K is higher than that of PdH. So the hydrogen isotope effect in PdH is reverse (negative). In contrast, the critical temperatures of the ThH and ThD compounds do not differ drastically from each other like those of PdH and PdD.

4   Physical properties of the third group of superconductors

In the previous section, superconducting materials were classified into three groups. The first group consists of conventional superconductors; the second comprises half-conventional ones, and unconventional superconductors form the third group. Assume that one day a room-temperature superconductor will become available. What group will it belong to? The answer is more or less obvious: to the third group of unconventional superconductors. Indeed, the highest critical temperature in third group of superconductors, $T_{c,max} \simeq 135$ K, is more than three times higher than that of the second group and more than one order of magnitude higher than that of group of conventional superconductors. Moreover, it seems that the critical temperatures of superconductors of the first and the second groups cannot exceed 10 K and 40 K, respectively. The third group of superconductors is the largest and has the highest rate of growth in the last twenty five years. If the rate of the growth of the third group will remain in the future at the same level, then, one will soon need to make an internal classification of this group.

From the discussion in the previous paragraph, it is evident that, in order to have guide to the properties of room-temperature superconductors, it is necessary to analyze the physical properties of superconductors of the third group, and not those of the first and second groups. One may argue, however, that room-temperature superconductors can form a separate group of superconductors, i.e. the fourth one. Generally speaking such a situation may occur, but there are only two options for a low-dimensional compound to be either magnetic or non-magnetic. As a consequence, every low-dimensional superconductor belongs either to the second or third group of superconductors.

Let us enumerate the common physical properties of superconductors of the third group. All superconductors of the third group:

- are magnetic or, at least, have strong magnetic correlations,

- are low-dimensional,

- have strongly correlated electrons/holes,

- are near a metal-insulator transition,

- are apparently near a quantum critical point,

- are type-II superconductors,

- have small-size Cooper pairs,

- have a low density of charge carriers, n_s,

- have a universal $n_s \propto \sigma(T_c)\dot{T}_c$ dependence [7], where $\sigma(T_c)$ is the *dc* conductivity just above T_c,

- have large values of H_{c2} and λ (magnetic penetration depth) and a large gap ratio $2\Delta_p/(k_B T_c)$, where Δ_p is the *pairing* energy gap (see Section 6),

- have anisotropic transport and magnetic properties,

- have a complex phase diagram (if there is a parameter to vary),

- have the moderately strong electron-phonon interaction,

- have an unstable lattice,

- have charge-donor and charge-acceptor sites (i.e. there is a charge transfer), and

- have a complex structure (with the exception of hydrides, deuterides and a few heavy fermions).

Among superconductors of the third group:

- the T_c value correlates with the behavior of spin fluctuations—the more dynamic the fluctuations are, the higher the T_c value is,

- the localized states in *undoped* material have spin-1/2 ground states,

- the average T_c value of layered compounds is higher than that of one-dimensional ones (even so, the transport properties of the layered compounds are quasi-one-dimensional),

- superconductors with $T_c > 20$ K have no metal-metal bonds (only heavy fermions have metal-metal bonds), and

- oxides and organic superconductors represent the absolute majority of the group.

At the same time, there are differences among superconductors of the third group. The two main differences are:

- the T_c value of hole-doped superconductors is on average a few times higher than that of electron-doped superconductors,

- the average T_c value of antiferromagnetic compounds is at least one order of magnitude higher than that of ferromagnetic superconductors.

Considering the common features of superconductors of the third group, one should realize that some of these features are direct consequences of the others. For example, the anisotropic character of transport and magnetic properties of superconductors of the third group is a direct consequence of a low-dimensional structure of these superconductors. The expression "systems with strongly correlated electrons" partially assumes that the electron-phonon interaction in these systems is sufficiently strong, and they have a complex phase diagram. The moderately strong electron-phonon interaction results in a large value of the pairing energy gap and, therefore, in a large value of the gap ratio $2\Delta_p/(k_B T_c)$. Since in superconductors of the third group, the Cooper pairs have a small size and a low density, this leads to the penetration depth and, consequently, the ratio λ/ξ to be large, where ξ is the coherence length. Therefore, all superconductors of the third group are type-II. The so-called Homes law, $n_s \propto \sigma(T_c)\dot{T}_c$, [7] literally means that an high-temperature superconductor should be a bad conductor just above T_c. The same conclusion follows from the other experimental fact that superconductivity with an high T_c occurs near a metal-insulator transition. Hence, some of these common features of superconductors of the third group are more important than others. Let us select the most important ones.

5   Requirements for high-T_c materials

We are now in a position to discuss the most important requirements for materials that superconduct at high temperatures. From the previous section, one can conclude that a room-temperature superconductor should:

- be hole-doped,

- be low-dimensional (preferentially, layered but with quasi-one-dimensional transport properties),

- be antiferromagnetic or, at least, have strong magnetic correlations,

- have strongly correlated holes,

- be near a metal-insulator Mott transition,

- have an *undoped* parent compound with the spin-1/2 localized states,

- have **dynamic** spin fluctuations,

- be in a state above a quantum critical point,

- have an unstable lattice,

- have a complex structure (i.e. with more than two sites per unit cell),

- have electron-acceptor sites, and

- have no metal-metal bonds.

It is necessary to comment on the issue of quantum critical point. In a quantum critical point where a magnetic order is about to form or to disappear, the spin fluctuations are the strongest. At the moment of writing, we do not know yet how to determine from a single measurement the presence/absence of a quantum critical point in a certain compound. So, this can be the first intermediate goal: how to determine quickly the presence/absence of a quantum critical point in a given compound.

In addition to these common features of the third group of superconductors, consider one more observation concerning the structure of good superconductors. In cuprates, the unit cell has three *interacting* subsystems: a quasi-metallic, a magnetic ones and charge reservoirs. The charge reservoirs in cuprates are the layers that intercalate the CuO_2 layers. After accepting/donating electrons, the charge reservoirs become semiconducting or insulating. The quasi-metallic and magnetic subsystems in cuprates are located into the CuO_2 planes, resulting in the phase separation. In organic superconductors, however, the second and the third subsystems coincide: the charge reservoirs, after donating/accepting electrons to/from organic molecules, become magnetic. For instance, the structure of a Bechgaard salt shown in Fig. 2 is a good example. Thus, in organic superconductors, one subsystem performs two functions. To summarize, a potential room-temperature superconductor should have:

    1) **a quasi-metallic subsystem**,
    2) **charge reservoirs**, and
    3) **magnetic atoms/molecules**.

Each subsystem should be coupled to the two others. Experimentally, the second and the third subsystems can be represented by the same atoms/molecules.

The requirements summarized in these section basically include Geballe's guidelines, described in Section 2. We shall use these hints in Sections 7–9.

6   Principles of superconductivity

Considering magnetic and structural requirements for materials, we should remember that the materials must superconduct after all. What does superconductivity as

a phenomenon require? Let us discuss in this section the main principles of super-conductivity as a phenomenon, valid for every superconductor independently of its characteristic properties and material. The underlying mechanisms of superconductivity can be different in various materials, but certain principles must be satisfied. One should however realize that the principles of superconductivity are not limited to those discussed in this section: it is possible that there are others which we do not know yet about. More detailed description of the principles of superconductivity can be found elsewhere [2, 3].

The first principle of superconductivity is:

Principle 1:   **Superconductivity requires quasiparticle pairing**

The electron (hole) pairs are known as Cooper pairs. In solids, superconductivity as a quantum state cannot occur without the presence of bosons. Fermions are not suitable for forming a quantum state since they have spin and, therefore, they obey the Pauli exclusion principle according to which two identical fermions cannot occupy the same quantum state. Electrons are fermions with a spin of 1/2, while the Cooper pairs are already composite bosons since the value of their total spin is either 0 or 1. Therefore, the electron (hole) pairing is an inseparable part of the phenomenon of superconductivity and, in any material, superconductivity cannot occur without quasiparticle pairing.

In the framework of the BCS theory [5], the electron pairing occurs in momentum space. However, for the occurrence of superconductivity in the general case, the electron pairing may take place not only in momentum space but also in real space. The electron pairing in momentum space can be considered as a *collective* phenomenon, while that in real space as *individual*. Independently of the space where they are paired—momentum or real—two electrons can form a bound state **only if** *the net force acting between them is attractive.*

Superconductivity requires the electron pairing and the Cooper-pair condensation. The second principle of superconductivity deals with the Cooper-pair condensation taking place at T_c. This process is also known as the onset of long-range phase coherence.

Principle 2:   **The transition into the superconducting state is the Bose-Einstein-like condensation and occurs in momentum space**

The two processes—the electron pairing and the onset of phase coherence—are independent of one another. Superconductivity requires both. In conventional superconductors, the pairing and the onset of phase coherence take place simultaneously at T_c. In many unconventional superconductors, quasiparticles become paired above T_c and start forming the superconducting condensate only at T_c.

In the 1920s, Einstein predicted that if an ideal gas of identical atoms, i.e.

bosons, at thermal equilibrium is trapped in a box, at sufficiently low temperatures the particles can in principle accumulate in the lowest energy level. This may take place only if the quantum wave packets of the particles overlap. In other words, the wavelengths of the matter waves associated with the particles—the *Broglie waves*—become similar in size to the mean particle distances in the box. If this happens, the particles condense, almost motionless, into the lowest quantum state, forming a Bose-Einstein condensate. The two condensates—superconducting and Bose-Einstein—have common quantum properties, but also, they have a few differences, which have been discussed elsewhere [2].

The third principle of superconductivity is:

Principle 3:   The mechanism of electron pairing and the mechanism of Cooper-pair condensation must be different

The validity of the third principle of superconductivity will be evident after the presentation of the fourth principle. Historically, this principle was introduced first. To recall, in conventional superconductors, phonons mediate the electron pairing, while the overlap of wavefunctions ensures the Cooper-pair condensation. Generally speaking, if in a superconductor, the same "mediator" (for example, phonons) is responsible for the electron pairing and for the onset of long-range phase coherence (Cooper-pair condensation), this will lead to the collapse of superconductivity.

If the first three principles of superconductivity do not deal with numbers, the forth principle can be used for making various estimations.

Generally speaking, a superconductor is characterized by a pairing energy gap Δ_p and a phase-coherence gap Δ_c. For genuine (not proximity-induced) superconductivity, the phase-coherence gap is proportional to T_c:

$$2\Delta_c = \Lambda\, k_B T_c, \tag{1}$$

where Λ is the coefficient proportionality, and k_B is the Boltzmann constant. At the same time, the pairing energy gap is proportional to the pairing temperature T_{pair}:

$$2\Delta_p = \Lambda'\, k_B T_{pair}. \tag{2}$$

Since the formation of Cooper pairs must precede the onset of long-range phase coherence, then in the general case, $T_{pair} \geq T_c$.

In conventional superconductors, however, there is only one energy gap Δ which is in fact a pairing gap but proportional to T_c:

$$2\Delta = \Lambda\, k_B T_c, \tag{3}$$

This is because, in conventional superconductors, the electron pairing and the onset of long-range phase coherence take place at the same temperature—at T_c. In all known cases, the coefficients Λ and Λ' lie in the interval between 3.2 and 6 (in one

heavy fermion, ~ 9) [2, 3]. We are now in position to discuss the fourth principle of superconductivity:

Principle 4: **For genuine, homogeneous superconductivity, $\Delta_p > \Delta_c > \frac{3}{4}k_B T_c$ always (in conventional superconductors, $\Delta > \frac{3}{4}k_B T_c$)**

The reason why superconductivity occurs exclusively at low temperatures is the presence of substantial thermal fluctuations at high temperatures. In conventional superconductors, the energy of electron binding, 2Δ, must be larger than the thermal energy; otherwise, the pairs will be broken up by thermal fluctuations. In the case of unconventional superconductors, the same reasoning is also applicable for the phase-coherence energy gap, Δ_c. The last inequality, $\Delta_p > \Delta_c$ for unconventional superconductors, means that the pairing energy $2\Delta_p$ of the Cooper pairs must be larger than the strength of the coupling of bosonic excitations responsible for mediating the long-range phase coherence with the Cooper pairs, which is measured by the energy $2\Delta_c$. If the strength of this coupling will exceed the pairing energy $2\Delta_p$, the Cooper pairs will immediately be broken up.

In the case $\Delta_p = \Delta_c$ occurring at some temperature $T < T_c$ remaining constant, locally there will be superconducting fluctuations due to thermal fluctuations, thus, a kind of inhomogeneous superconductivity. It is necessary to mention that the case $\Delta_p = \Delta_c$ must not be confused with the case $T_{pair} = T_c$, because usually $\Lambda' > \Lambda$.

Finally, let us go back to the third principle of superconductivity to show its validity. The case in which the same bosonic excitations mediate the electron pairing **and** the phase coherence is equivalent to the case $\Delta_p = \Delta_c$ discussed above. Since, in this particular case, the equality $\Delta_p = \Delta_c$ is independent of temperature, the occurrence of homogeneous superconductivity is impossible.

7   An approach to room-temperature superconductivity

Approaching the problem of room-temperature superconductivity, different researchers can use the information presented above in different ways: human imagination does not have limits. One approach, however, is more or less obvious. The structure of cuprates basically satisfies all the requirements described above. Then, one can replace the CuO_2 planes by planes of different type, which can accommodate, depending on the doping level, the Cooper pairs and antiferromagnetic ordering above room temperature. The only problem is that one should know what type of planes to use.

Another possibility is to use the structure of organic salts shown in Fig. 2 as the basis for the structure of new superconductors. Luckily, the issue of the presence of Cooper pairs in some organic compounds above room temperature is known already for some time. In addition to substitution of the organic molecules, the magnetic molecules of PF_6 in Fig. 2 should be replaced by other type of molecules which are

ordered antiferromagnetically above room temperature. To the end of this chapter, we shall explore this approach to the problem.

8 Organic molecules, polymers and tissues with electron pairs above room temperature

According to the first principle of superconductivity, superconductivity requires electron pairing. Indeed, the electron pairing is the keystone of superconductivity. Therefore, in quest of compounds that superconduct above room temperature, one should first look at materials which tolerate the presence of Cooper pairs at high temperatures. Fortunately, it is known already for some time that the Cooper pairs exist in some organic compounds at and above room temperature. In this section we are going to discuss these organic materials. It is worth to mention, however, that superconductivity does not occur in these compounds because superconductivity requires not only electron pairing but also the establishment of long-range phase coherence.

The idea to use organic compounds as superconducting materials is not new. In 1964, Little proposed a model in which a high T_c is obtained due to a non-phonon mediated mechanism of electron attraction, namely, an *exciton* model for Cooper-pair formation in long chainlike organic molecules [8]. In the framework of his model, the maximum critical temperature was estimated to be around 2200 K! Little's paper has encouraged the search for room-temperature superconductivity, especially in organic compounds.

8.1 Organic molecules

In 1975, Kresin and co-workers showed that the superconducting-like state exists *locally* in complex organic molecules with conjugate bonds [9]. Figure 3 shows a few examples of such molecules. Their main building blocks are carbon and hydrogen atoms. The characteristic feature of these conjugated hydrocarbons is the presence of a large number of π electrons. These collectivized electrons are in the field of the so-called σ electrons which are located close to the atomic nuclei and not much different from the ordinary atomic electrons. At the same time, the π electrons are not localized near any particular atom, and they can travel throughout the entire molecular frame. This makes the molecule very similar to a metal. The framework of atoms plays the role of a crystal lattice, while the π electrons that of the conduction electrons. It turns out, in fact, that the conjugated hydrocarbons with even number of carbon atoms are more than just similar to a metal, but are actually small superconductors [9]. Experimentally, conjugated hydrocarbons with even number of carbon atoms (thus, with even number of π electrons) exhibit properties similar to those of a superconductor: the Meissner-like effect, zero resistivity and the presence of an energy gap. The π electrons form
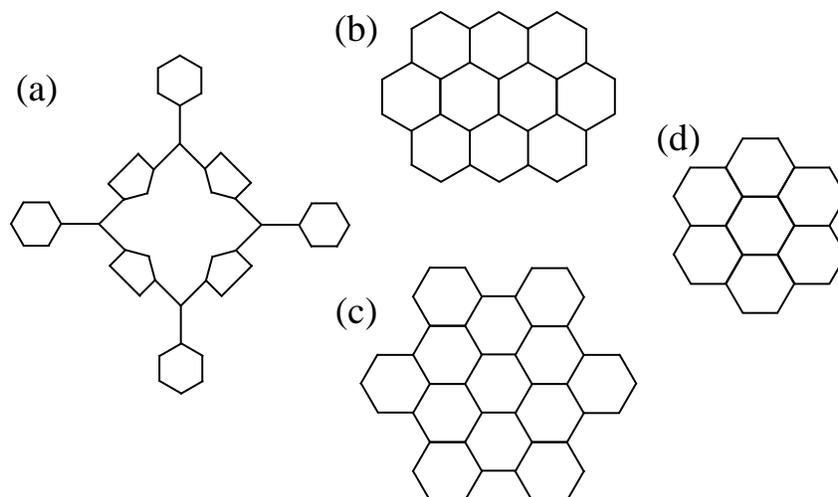
Figure 3: Organic molecules with delocalized π electrons: (a) tetraphenylporphin; (b) ovalene; (c) hexabenzocoronene, and (d) coronene [9].

bound pairs analogous to the Cooper pairs in an ordinary superconductor. The pair correlation mechanism is principally due to two effects: (i) the polarization of the σ electrons, and (ii) $\sigma - \pi$ virtual electron transitions. However, if the number of π electrons is odd, the properties of such conjugated hydrocarbons are different from those of a superconductor.

• The alkali-doped fullerenes discussed in Section 3 are able to superconduct but they are electron-doped. To exhibit room-temperature superconductivity, the single crystals of C_{60} must be doped by holes. Thus, one should find suitable dopant species for this purpose. Theoretical calculations show that fullerenes having a diameter smaller than that of C_{60}, such as C_{28} and C_{20}, are able to exhibit a higher value of T_c relative to that of C_{60} [2]. Unlike graphene and other long organic polymers, the fullerenes have an advantage to be packed into any form.

One can use fullerenes not only in pure but also in polymerized form. As an example, Figure 4 shows various one- and two-dimensional polymeric solids formed from C_{60}.

• As discussed in Section 3, carbon nanotubes can be viewed as giant conjugated molecules with a conjugated length corresponding to the whole length of the tube. The nanotubes are also a promising candidate with which to form a room-temperature superconductor.

The single-walled carbon nanotubes with a diameter of 4.2 ± 0.2 Å exhibit *bulk* superconductivity below $T_c \simeq 15$ K. The nanotubes with a smaller diameter may display a higher T_c. The onset of *local* superconductivity at 645 K was observed in single-walled carbon nanotubes containing a small amount of the magnetic impurities Ni:Co (≤ 1.3 %) [11]. This unconfirmed evidence is based on transport,
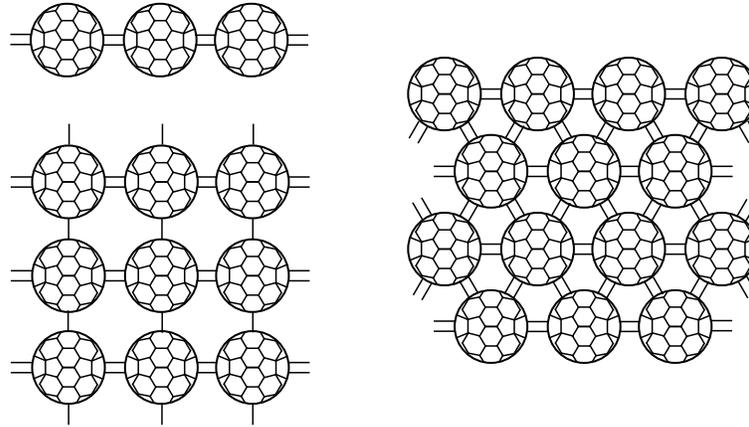
Figure 4: Various one- and two-dimensional polymeric solids formed from C_{60} [10]. The C_{60} balls are shown schematically.

magnetoresistance, tunneling and Raman measurements. In single-walled carbon nanotubes, the energy gap obtained in tunneling measurements is about $\Delta_p \simeq 100$ meV [11]. By embedding these nanotubes into a *dynamic* magnetic medium, one can witness bulk superconductivity above 450 K. Thus, in the general case, in order to accommodate the pairs at high temperatures, nanotubes should be *doped* or contain *defects*.

8.2   Organic conjugated polymers

Polythiophene is a one-dimensional conjugated polymer. Figure 5(a) shows its structure. It has been known already for some time that, in polythiophene, the dominant nonlinear excitations are positively-charged polarons and bipolarons [12]. This means that the Cooper pairs with a charge of $+2|e|$ exist at room temperature in polythiophene. Figure 5(b) depicts a schematic structural diagram of a bipolaron on a polythiophene chain. In a thiophene ring, the four carbon p electrons and the two sulfur p electrons provide the six p electrons that satisfy the $(4n + 2)$ condition necessary for aromatic stabilization. Polythiophene has a few derivatives and one of them shown in Fig. 5(c) is called poly(3-alkylthienylenes) or P3AT for short. In contrast to polythiophene, P3AT is soluble.

Polythiophene chains have the infinite length. Polythiophene chains having a finite length can be used too. However, the ends of the pieces of the polymer must be "closed." Alternatively, the two ends of a polymer piece can be attached one to another leading to the formation of a ring. Taking into account that the width of a bipolaron is a few lattice constants; then, the length of pieces of polythiophene chains, ℓ, should be 2–3 times larger; thus $\ell \sim 15a$, where a is the lattice constant.

Other conjugated polymers also contain bipolarons. It is known that positively-
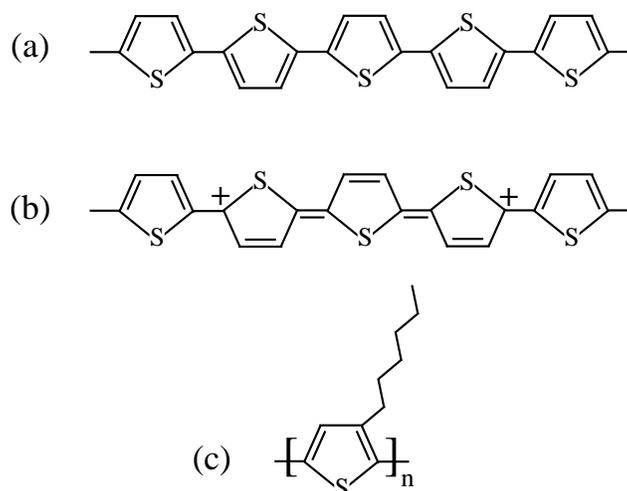
Figure 5: (a) Chemical structure of polythiophene. (b) Schematic structural diagram of a positively-charged polaron on a polythiophene chain. (c) Chemical structure of soluble poly(3-alkylthienylenes) [12].

charged bipolarons exist, for example, in polyparaphenylene, polypyrrole and poly(2,5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT) [12]. The structure of polyparaphenylene is depicted in Fig. 6(a). A bipolaron on a polyparaphenylene chain is schematically shown in Fig. 6(b). One of the derivatives of polyparaphenylene, *p*-sexiphenyl depicted in Fig. 6(c). The structure of PDHPT is illustrated in Fig. 6(d). Bipolarons have also been observed in other one-dimensional conjugated organic polymers such as polyparaphenylene and polypyrrole [12]. A large number of conjugated polymers used in electroluminescent diodes at room temperature contain bipolarons, such as poly(*p*-phenylene vinylene) etc., (see Fig. 2 in [13]). All these polymers are commercially available.

8.3   Living tissues

It is known that (i) in redox reactions occurring in living organisms, electrons are transferred from one molecule to another in pairs with opposite spins; and (ii) electron transport in the synthesis process of ATP (adenosine triphosphate) molecules in conjugate membranes of mitochondria and chloroplasts is realized by pairs, not individually [14, 15, 16].

In living tissues, the electron pairing simplifies their propagation because the calculations show that, for electrons, it is more profitable *energetically* to propagate together than separately, one by one [15]. So, the electron pairing occurs in living tissues first of all because of an energy gain; the electron spin is a secondary reason for the pairing. However, we are more interested in electron pairing because of spin.
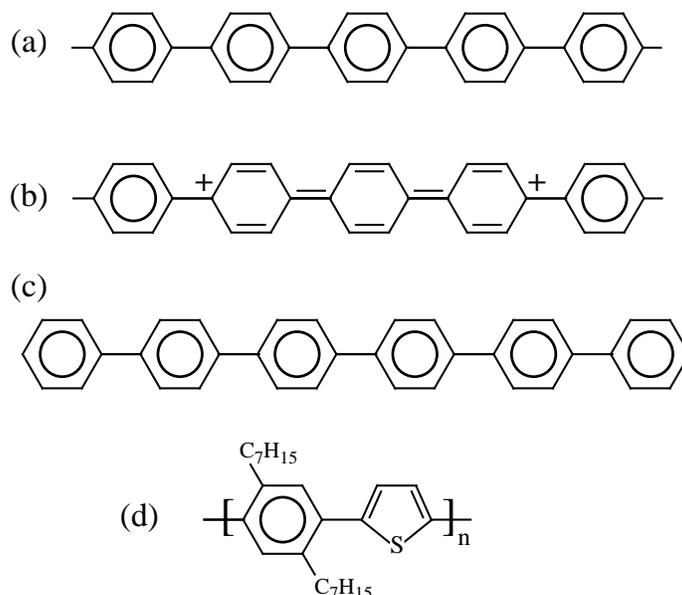
Figure 6: (a) Chemical structure of polyparaphenylene. (b) Schematic structural diagram of a positively-charged bisoliton on a polyparaphenylene chain [12]. (c) Molecular structure of p-sexiphenyl, and (d) the chemical structure of soluble poly(2,5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT).

The body temperature of living creatures is usually near the room temperature. Therefore, one can use these materials to form a room-temperature superconductor. As discussed earlier, superconductivity does not occur in living tissues because, according to the principles of superconductivity, it requires not only the electron pairing but also the onset of long-range phase coherence.

Recently, living organisms have been found in extreme conditions: some survive without sunlight, some survive in water near the boiling point. Probably the most extreme case is the discovery of so-called black smokers or chimneys on the ocean floor. Deep-sea vents provide an unusual habitat for some primitive forms of extremophile bacteria and deep-sea crabs that can survive extreme conditions. For example, the *Spire* vent is located at the Broken Spur Vent Field in the Mid-Atlantic Ridge, 3080 m below sea level. The measurement of water temperature at which the crabs reside there yielded $T \sim 365$ C. This means that the electron pairs exist in certain organic materials at temperatures above 600 K.

Mitochondria and chloroplasts are integral parts of almost every living cell. In principle, one can easily use their membranes to form a room-temperature superconductor. The redox reactions occur practically in every cell. One should find out what parts of the cells are responsible for the redox reactions, and then use these tissues. The living tissues are usually one- or two-dimensional.

Other living tissues may also contain bipolarons. Nowadays it is known that, in the living matter, the signal transfer occurs due to charge (electron) transfer. It is possible that, in *some* cases, the electron transfer occurs in pairs with opposite spins.

Pullman and Pullman already in 1963 emphasized that "the essential fluidity of life agrees with the fluidity of the electronic cloud in conjugated molecules. Such systems may thus be considered as both the cradle and the main backbone of life" [17]. Indeed, all natural molecules are conjugated [18], and it is possible that, some of them can be used to synthesize a room temperature superconductor.

8.3.1   Graphite

For the last forty years, graphite is one of the most studied materials (see, e.g. [19]). It is also one of the **most** promising superconducting materials. Graphite intercalation compounds (GICs) able to superconduct were discussed in Section 3. All superconducting GICs are alkali-doped and, therefore, magnetic due to alkali spins ordered antiferromagnetically. In the superconducting GICs, the charge carriers are however electrons, not holes.

There exist both theoretical predictions and experimental evidence that electronic instabilities in pure graphite can lead to the occurrence of superconductivity and ferromagnetism, even at room temperature [20]. In graphite, an intrinsic origin of high-temperature superconductivity relates to a **topological disorder** in graphene layers [20]. This disorder enhances the density of states at the Fermi level. For example, four hexagons in graphene can in principle be replaced by two pentagons and two heptagons. Such a defect in graphene modifies its band structure. In real space, the disorder in graphene transforms an ideal two-dimensional layer into a network of quasi-one-dimensional channels.

In practice, the graphene sheets are always finite. Their electronic properties are drastically different from those of bulk graphite. It is experimentally established that the electronic properties of nanometer-scale graphite are strongly affected by the structure of its edges [20]. The graphene edges induce electronic states near the Fermi level. Any graphene edge can be presented by a linear combination of the two basic edges: zigzag and armchair, shown in Fig. 7. The free energy of an armchair edge is lower than that of a zigzag edge.

The appearance of bipolarons at high temperatures in graphene depends on the graphene structure: graphene sheets must be topologically disordered. As mentioned above, one can replace some hexagons in graphene by pentagons and heptagons. Alternatively, some carbon atoms in graphene can be substituted for B, N or Al (B and Al are probably better than N because each N adds an additional electron to graphene, while room-temperature superconductivity requires holes). Instead of graphene sheets, one can for instance use nanostripes of graphene. Since the bonds between adjacent layers in graphite are weak, individual atomic graphene planes can be pulled out of bulk crystals [21] and be used further.
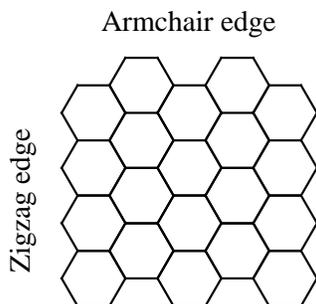
Armchair edge

Figure 7: Two basic types of graphite edges.

In principle, it should be not a problem for bipolarons to occur in graphite and graphene-based compounds above room temperature. The main problem for the occurrence of bulk superconductivity in graphite and other organic compounds above room temperature is the onset of long-range phase coherence. One can dope graphite by atoms/molecules, spins of which are ordered antiferromagnetically after the diffusion. This issue will be discussed in the following section.

At the end, it is worth noting that materials which contain bipolarons above room temperature are not limited to those discussed in this section. It is possible that there are compounds which tolerate the presence of bipolarons above room temperature but are unknown to us at the moment of the writing.

9   Structure and constituents of a potential room-temperature superconductor

As discussed in Section 7, the structure of a Bechgaard salt shown in Fig. 2 basically satisfies all the requirements for materials that superconduct at high temperatures, which are described in Section 5. In superconducting organic salts, the Cooper pairs reside on organic molecules organized in stacks, which are shown in Fig. 1. The stacks form one-dimensional structures similar to those in Fig. 2. In the crystal, the chains of other atoms or molecules (e.g. PF_6, ClO_4 etc.) are situated between the stacks and aligned parallel to them, as shown in Fig. 2. The organic molecules donate electrons to the anions, which prefer to order antiferromagnetically. In some organic salts, e.g. in the BEDT-TTF family, the arrays of organic molecules form conducting layers separated by insulating anion sheets. So, in contrast to the Bechgaard salts which exhibit quasi-one-dimensional electron transport, the electronic structure of the BEDT-TTF family is two-dimensional.

As suggested in Section 7, the idea to create a compound able to superconduct above room temperature is straightforward. Taking the crystal structure of the Bechgaard salt shown in Fig. 2 as a basis, one should replace the stacks of the organic TMTSF molecules by molecules/polymers/layers of a certain material which

contains the Cooper pairs above room temperature. At the same time, the molecules of PF_6 in Fig. 2 should be substituted for other atoms or molecules which are able to accept electrons from the conducting counterparts and to become antiferromagnetically ordered above room temperature. Also, one can add a small amount of atoms/molecules which stand duty *exclusively* as charge reservoirs. So, the basic idea is more or less obvious; the main question is what materials to use and how to achieve the right intercalation.

Materials which contain bipolarons above room temperature have been discussed in the previous section. As a matter of fact, they are all organic. What is about atoms/molecules which are magnetic in the intercalated state?

A superconductor of the third group must be magnetic or, at least, have strong magnetic correlations. While oxides can be magnetic naturally, like cuprates for example, organic and living-tissue-based compounds must be doped by magnetic species. Unfortunately, during evolution, Nature did not need to develop such magnetic materials. Hence, one should only rely on accumulated scientific experience and work by trial and error.

By doping organic materials or living tissues, one should take into account that, after the diffusion, the dopant species must not be situated too close to the organic molecules/tissues. Otherwise, they will have a strong influence on bipolaron wavefunctions and may even break up the bipolarons. On the other hand, the dopant species cannot be situated too far from the organic molecules/tissues because, as the common logic suggests, bipolarons should be coupled to spin fluctuations. Therefore, synthesizing a room-temperature superconductor, one must pay attention to its structure: the "distance" between failure and success can be as small as 0.01 Å in the lattice constant.

What materials can be used as the acceptors of electrons? From experience [2], materials able to accept electrons from organic molecules are the following atoms and molecules: Cs, I, Br, PF_6, ClO_4, $FeCl_4$, $Cu(NCS)_2$, $Cu[N(CN)_2]Br$ and $Cu[N(CN)_2]Cl$. However, in existing superconducting organic salts, they are ordered antiferromagnetically at low temperatures, and it is not obvious at all, if they are able to behave in the same way above room temperature. As discussed in Section 5, in a superconductor of the third group, spin fluctuations should be dynamic. As a matter of fact, the dynamic character of spin fluctuations can be achieved artificially, as suggested elsewhere [2].

At the end of this section, a few remarks about the structure of a potential room-temperature superconductor should be made. As an example, consider polythiophene. Polythiophene, its derivatives and other organic conjugated polymers are usually doped by using the so-called electrochemical method [12]. The reaction is carried out at room temperature in an electrochemical cell with the polymer as one electrode. To remove electrons from organic polymers, oxidation is usually used. Through doping, one can control the chemical potential. In practice, however, it is impossible to foresee the structure of a doped organic compound, even knowing
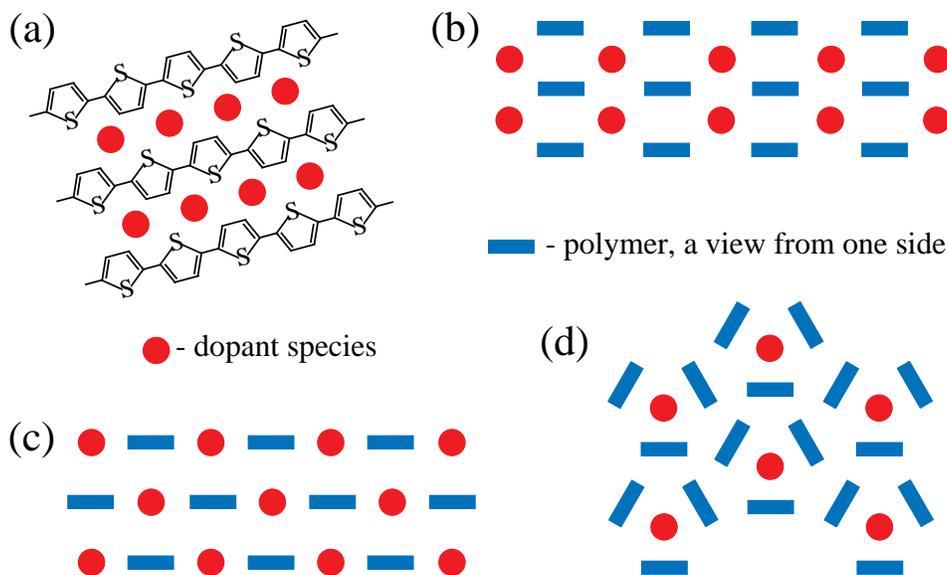
Figure 8: Possible positions of dopant species relative to infinite polythiophene chains: (a) in the plane of polythiophene chains; (b) between the planes; (c) a checker-border pattern, and (d) a "triangular" pattern realized in Na-doped poly-acetylene [12].

materials before the beginning of the doping procedure. Depending on their origin, concentration and size, the dopant species after the diffusion can take different positions relative to the polythiophene chains. Figure 8 shows several examples of possible positions of dopant species relative to polythiophene chains. Upon doping, the polythiophene chains and dopant species can, for example, be in-plane, as sketched in Fig. 8(a), or alternate, as illustrated in Fig. 8(b). They can, for example, form a checker-board pattern shown schematically in Fig. 8(c). For instance, in Na-doped polyacetylene, the Na^+ ions and polyacetylene chains form a modulated lattice with a "triangular" pattern depicted in Fig. 8(d). In Na-doped polyacetylene, such a lattice appears exclusively at moderate doping levels.

Using various magnetic atoms/molecules, one should not forget to control the doping level of the organic polymers. It can be done, for example, by adding a small amount of atoms/molecules of another type, which may or may not be magnetic after the diffusion. Undoubtedly, some of these doped polythiophene-chain materials will superconduct. The main question is what maximum value of T_c can be attained in these organic compounds.

From the discussions in this section, one can make an important conclusion, namely that, *for the occurrence of superconductivity at room temperature, the onset of long-range phase coherence will be the bottleneck, not the quasiparticle pairing.*

In the case of graphene or other two-dimensional materials, an alternative way

to create a room-temperature superconductor can be suggested. One can dope graphene directly by species which become antiferromagnetically ordered in the doped state above room temperature, and induce the states at the Fermi level.

10   Conclusions

This chapter presents analysis of experimental data. On the basis of this analysis, it is possible to draw conclusions about components and the structure of a superconductor with a critical temperature which may exceed the room temperature. The two essential components of a promising room-temperature superconductor are large organic molecules (polymers, tissues) and atoms/molecules which are magnetic in the intercalated state. To reach this conclusion, one does not require knowledge of the mechanism of room-temperature superconductivity. However, to synthesize a room-temperature superconductor is a very difficult task and, in a first approximation, equivalent to the task of finding a needle in a haystack. Nevertheless, the importance of this chapter is in that it indicates in which "haystack" to search.

11   A note about the mechanism of superconductivity in cuprates

It is possible that in cuprates there are two more or less independent processes, leading to the occurrence of high-T_c superconductivity. One of them is the formation of incoherent electron (hole) pairs, and the second process is the Bose-Einstein condensation of magnetic excitations, for example, magnons. Recently, the Bose-Einstein condensation of magnons was observed in a number of antiferromagnetic compounds [22]. If the Cooper pairs are coupled to magnetic excitations, then the pairs can adjust their phases, i.e. establish the long-range phase coherence, through the long-range phase coherence of the magnon Bose-Einstein condensate. The Cooper pairs can be coupled to magnetic excitations through the amplitude of their wavefunctions, or only through the phase, or through both.

References

[1] Kamerlingh Onnes, H. *Commun. Phys. Lab. Univ. Leiden* 1911, **124c**.

[2] Mourachkine, A. *Room-Temperature Superconductivity*; Cambridge International Science Publishing: Cambridge, 2004, pp 12, 71, 81, 129, 136, 285, 107, 293 (also http://arxiv.org/ftp/cond-mat/papers/0606/0606187.pdf).

[3] Mourachkine, A. *High-Temperature Superconductivity in Cuprates: The Nonlinear Mechanism and Tunneling Measurements*; Kluwer Academic Publishers: Dordrecht, 2002, pp 247, 246,

[4] Geballe, T. H. *Science* 1993, **259**, 1550.

[5] Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. *Phys. Rev.* 1957, **108**, 1175.

[6] Weller, T. E.; Ellerby, M.; Saxena, S. S.; Smith, R. P.; Skipper N. T. *Nature Physics* 2005, **1**, 39.

[7] Homes, C. C.; Dordevic, S. V.; Strongin, M.; Bonn, D. A.; Liang Ruixing; Hardy W. N.; Komiya Seiki; Ando Y.; Yu, G.; Kaneko, N.; Zhao, X.; Creven, M.; Basov, D. N.; Timusk, T. *Nature* 2004, **430**, 539.

[8] Little, W. A. *Phys. Rev.* 1964, **134**, A1416.

[9] Kresin, V. Z.; Litovchenko, V. A.; Panasenko, A. G. *J. Chem. Phys.* 1975, **63**, 3613.

[10] Andriotis, A. N.; Menon, M.; Sheetz, R. M.; Chernozatonskii, L. *Phys. Rev. Lett.* 2003, **90**, 026801.

[11] Zhao, G.-m. preprint 2000, cond-mat/0208200.

[12] Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* 1988, **60**, 781.

[13] Friend R. H.; Gymer R. W.; Holmes A. B.; Burroughes J. H.; Marks R. N.; Taliani C.; Bradley D. D. C.; Dos Santos D. A.; Brédas J. L.; Lögdlund M.; Salaneck W. R. *Nature* 1999, **397**, 121.

[14] Davydov, A. S. *Solitons in Molecular Systems*; *Naukova Dumka*: Kiev, 1988 (in Russian), p. 103.

[15] Davydov, A. S. *Phys. Rep.* 1990, **190**, 191.

[16] Davydov, A. S. *Solitons in Molecular Systems*; Kluwer Academic Publishers: Dordrecht, 1991, p. 124.

[17] Pullman, B.; Pullman, A. *Quantum Biochemistry*; Interscience: New York, 1963.

[18] Clardy, J.; Walsh, C. *Nature* 2004, **432**, 829.

[19] *Graphite Intercalation Compounds*, Tanuma, S. and Kamimura, H.; Ed.; World Scientific: Singapore, 1985.

[20] Kopelevih, Y.; Esquinazi, P.; Torres, J. H.; da Silva, R. R.; Kempa, H.; Mrowka, F.; Ocana, R. preprint 2002 (a chapter in a book), cond-mat/0209442, and references therein.

[21] Novoselov, K. S.; Jiang, D.; Booth, T.; Khotkevich, V. V.; Morozov, S. M.; Geim, A. K. *PNAS* 2005, **102**, 10451.

[22] See, for example, Ruegg, Ch.; Cavadini, N.; Furrer, A.; Gudel, H.-U.; Kramer, K.; Mutka, H.; Wildes, A.; Habicht, K.; Vorderwisch, V. *Nature* 2003, **423**, 62.