Abstract
Superconductivity was discovered by Kamerlingh Onnes in 1911. He noticed that the resistance of mercury suddenly drops to zero at 4.2 K. Until 1986 critical temperatures were limited to low values not exceeding 30 K. In year 1986 Bednorz and Müller discovered high temperature superconductivity in cuprates with critical temperature higher than 100 K. After this discovery, a search for new high temperature superconducting families began and it lead to the discovery of layered iron-pnictide compounds with critical temperatures limited to 50 K. They share many similarities with cuprates among them: layered structure, antiferromagnetic phases next to superconductivity and unusually low conductivity in the normal state. Here we review some of the most important physical properties of this new family.
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1 Superconductivity

Superconductivity occurs when electrical resistivity of the specimen drops to zero when cooled to a sufficiently low temperature also known as critical (transition) temperature, $T_C$. Below $T_C$ resistivity is zero, not just close to zero. This was, for instance, demonstrated by injecting current into lead superconducting (SC) wire. This SC current persists almost indefinitely as long as $T < T_C$. In Figure 1 we show the historical electrical measurement of Kamerlingh Onnes, who first reported on a discovery of superconductivity in mercury in 1911. Transition temperature for mercury is 4.2 K (Figure 1).

![Figure 1: Resistance in ohms of a specimen of mercury versus absolute temperature by Kamerlingh Onnes in 1911 [1].](image)

2 Properties of superconductors

Zero resistivity measurements are usually not sufficient to claim that studied compound is superconducting. Ultimate proof for superconductivity is due to the Meissner-Ochsenfeld effect (Figure 2).


2.1 Meissner-Ochsenfeld effect

When the specimen is placed in a magnetic field, and then cooled, the magnetic flux is expelled from the specimen (Figure 3). This is known as Meissner effect. If there would be any magnetic field in superconductor it would change the flux. According to Lenz’s law a current would be generated, which would oppose the flux, and eject any magnetic field from the superconductor. For the case, when magnetic field is expelled from the specimen, we can write

\[ B = 0 = \mu_0 (H + M) = \mu_0 H (1 + \chi). \]  

(1)

Here \( M \) is magnetization and \( \chi \) is magnetic susceptibility. Because there is no magnetic field in specimen we can see from equation (1) that \( \chi = -1 \). A superconductor in magnetic field will act as a perfect diamagnet.
2.2 London equation describes Meissner effect

London equation can correctly predict magnetic field penetration into the SC material, but cannot give a microscopic picture. Let us assume a two-fluid model [4], where we distinguish between normal electrons and superconducting electrons \( n = n_N + n_S \), where \( n \) is the electron density. As it was proven by the BCS theory, \( n_S \) are Cooper pairs, which are bound states of electron pairs. For superconducting electrons in electric field we can write

\[
m \frac{d\mathbf{v}_S}{dt} = -e_0 \mathbf{E}.
\] (2)

If we consider equation for current density and apply it for superconducting electrons

\[
\mathbf{j}_S = -e_0 n_S \mathbf{v}_S,
\] (3)

we get

\[
\frac{dj_S}{dt} = \frac{n_S e_0^2}{m} \mathbf{E}.
\] (4)

Combining this with Faraday’s law \( \nabla \times \mathbf{E} = -\partial \mathbf{B}/\partial t \) we obtain

\[
\frac{\partial}{\partial t} \left( \nabla \times \mathbf{j}_S + \frac{n_S e_0^2}{m} \mathbf{B} \right) = 0.
\] (5)

At this stage Fritz London took into account also the Meissner’s effect i.e. that the magnetic field in superconductor is zero, and derived

\[
\nabla \times \mathbf{j}_S = -\frac{n_S e_0^2}{m} \mathbf{B}.
\] (6)

If equation (6) is combined with \( \nabla \times \mathbf{B} = \mu_0 \mathbf{j}_S \) we get

\[
\nabla^2 \mathbf{B} = \frac{\mu_0 n_S e_0^2}{m} \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B} \implies B(x) = B_0 \exp \left( -\frac{x}{\lambda} \right),
\] (7)

where \( \lambda = \sqrt{m/\mu_0 n_S e_0^2} \) is a London penetration depth, which measures the depth of penetration of the magnetic field. Inserting typical values for the density of SC charges we find that for standard superconductors it is in order of 10 nm, while in HTSC it is around 100 nm.

2.3 Coherence length

In experiment beside London penetration depth \( \lambda \) we also measure the coherence length \( \xi \). The coherence length is a measure of the distance within which
the superconducting electron pairs cannot change drastically in a spatially-varying magnetic field.

Pippard has proposed a modification of the London equation in which the current density at a point is given by an integral of the vector potential over a region surrounding the point [5]

\[
\mathbf{j}(\mathbf{r}) = -\frac{3}{4\pi\epsilon_0 \Lambda \xi_0} \int \frac{\mathbf{R} \cdot \mathbf{A}(\mathbf{r}')}{R^4} e^{-R/\xi_0} d\tau',
\]

where \( \Lambda = m/ne^2 \), \( n \) is the number of superconducting electrons, \( \mathbf{R} = \mathbf{r} - \mathbf{r}' \) and \( \xi_0 \) is coherence length. The BCS theory [5] evaluates the spatial distribution of the current density and exhibit it in a form similar to that proposed by Pippard. They wrote coherence length as

\[
\xi_0 = \frac{\hbar v_0}{\pi E_0} = 0.18 \frac{\hbar v_0}{kT_C},
\]

where \( v_0 \) is average velocity of electrons at Fermi surface and 0.18 is the theoretical value. Coherence length is in order of 100 nm for ”standard” SC and about 1 nm for HTSC (Table 2, page 13) [3].

2.4 Type I and type II superconductors

The superconducting state in specimen is destroyed if the specimen is placed in a sufficiently strong magnetic field (critical field, \( H_c \)) or if we generate strong enough currents (critical current \( > 10^5 \) A/cm²). Based on this we distinguish two types of superconductors: type I and type II. Type I superconductor expels a magnetic field for \( H < H_c \) while for \( H > H_c \) superconductivity is destroyed and the field penetrates completely into the sample (Figure 4). A type II superconductor expels field in the normal state completely under \( H_{c1} \). When \( H \) exceeds \( H_{c1} \) the field is only partially excluded, and the bulk specimen remains to be superconducting. Between \( H_{c1} \) and \( H_{c2} \) the superconducting state coexists with normal state regions where magnetic field penetrates into the sample. Field uniformly penetrates specimen in form of vortices (Figure 6). This mixed state is called vortex state. Vortex state describes swirling tubes of electrical current induced by an external magnetic field which penetrates into the surface of a superconducting material. Inside the vortices the specimen is in the normal state surrounded by the superconducting state. Above field \( H_{c2} \) the flux penetrates completely and superconductivity vanishes.
An important difference in type I and type II superconductor is in the mean free path of the conducting electrons in the normal state. If the coherence length $\xi$ is longer than the penetration depth $\lambda$, the superconductor will be type I. When the mean free path is short, then the $\xi$ is also short and the $\lambda$ is large, so the superconductor will be type II. A type II superconductor is also characterized by a vortex state (Figure 5) stable over a certain range of magnetic field strength between $H_{c1}$ and $H_{c2}$. Quantization of the magnetic flux through one vortex is [3]

$$\phi_0 = \frac{n}{2e} \frac{h}{}. \quad (8)$$

Flux $\phi_0$ is quantized as $n$ is the integer number of vortices. Field will extend from normal core into the superconducting environment to a distance equal to $\lambda$ [3]. The flux associated with single vortex is $\pi \lambda^2 H_{c1}$, and this must be
equal to $\phi_0$. Thus

$$H_{c1} \approx n\frac{\hbar}{e\lambda^2}. \quad (9)$$

At $H_{c2}$ the vortexes are packed as densely as the coherence length $\xi$ will allow. The external field penetrates the specimen almost uniformly. Each vortex is responsible for carrying a flux of the order $\pi\xi^2 H_{c2}$, which is also quantized to $\phi_0$. Thus

$$H_{c2} \approx \frac{\hbar}{e\xi^2}. \quad (10)$$
gives the estimation of upper critical field. Using typical values for "standard" superconductor ($\lambda \sim 100$ nm, $\xi \sim 1$ nm) we can estimate:

$$H_{c1} \approx 0.66 \text{ T and } H_{c2} \approx 6.6 \text{ T.}$$

3 BCS theory

The BCS theory was developed by Bardeen, Cooper and Schrieffer in 1957 to quantum-mechanically treat superconductivity. With a microscopic model BCS theory successfully describes all properties of superconductors: attractive effective electron-electron interaction to form Cooper pairs, role of lattice vibrations, and predicts transition temperature below which the superconductivity accours. A phonon model states that the first electron interacts with the lattice and deforms it. A second electron feels the deformed lattice (even when the first electron has already moved away - retardation effect) and adjusts itself to take the most advantage of the deformation to lower its energy. In this way the second electron interacts with the first via the lattice vibrations (phonons) [5]. The transition temperature for $UD(E_F) \ll 1$ the theory predicts

$$T_C = 1.14\Theta \exp \left(-\frac{1}{UD(E_F)}\right), \quad (11)$$

where $\Theta = h\omega_D/(2\pi k_B)$ is Debeye temperature. Inserting typical values for $U$, $D$ and $\Theta$ in equation (11) one can estimate, that $T_C$ should not be higher than 30 K [3].

4 High temperature superconductivity

Bednorz and Müller discovered high temperature superconductivity in 1986. In few years many copper oxide (cuprates) high temperature superconductors (HTSC) were synthesized. The highest $T_C$ was reported for thallium doped, mercury based cuprate with critical temperature at 138 K.
High transition temperatures in HTSC clearly exceed predictions made by BCS theory for maximal $T_C$ as we can see in Table 2. High temperature superconductors are layered copper oxide phases with high transition temperatures exceeding 100 K and high magnetic field as high as 100 T. They are type II superconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_C$ [K]</th>
<th>$\lambda$ [nm]</th>
<th>$\xi$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg$<em>{12}$Tl$<em>3$Ba$</em>{30}$Ca$</em>{30}$Cu$<em>{45}$O$</em>{127}$</td>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>5$O$</em>{10}$</td>
<td>110</td>
<td>260</td>
<td>1.5</td>
</tr>
<tr>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>92</td>
<td>150</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1: High temperature Cu-oxides with critical temperatures.

<table>
<thead>
<tr>
<th></th>
<th>low temperature SCs</th>
<th>HTSCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration depth $\lambda$</td>
<td>$\sim$10 nm</td>
<td>$\sim$100 nm</td>
</tr>
<tr>
<td>Coherence length $\xi$</td>
<td>$\sim$100 nm</td>
<td>$\sim$1 nm</td>
</tr>
</tbody>
</table>

Table 2: Comparison between low temperature SCs and HTSCs.

4.1 Structure

The crystal structures are oxygen-defect modifications of the perovskite structure (Figure 6 (a)). Defect refers to vacant lattice sites. Perovskites are large family of crystalline ceramics with a metal to oxygen ratio of approximately 2 to 3. The general formulation of perovskite structures is $AXO_3$, where $A$ is a metal ion with a +2 valence and $X$ is a metal with +4 valence. Parallel superconducting layers of CuO$_2$, insulating layers and hole donating layers are structural feature of all HTSC with $T_C > 40$ K. They contain few charge carriers compared to normal metals, and display highly anisotropic electrical and magnetic properties which are very sensitive to oxygen content.

4.2 Phase diagram

Unusual behavior of HTSC can be summarized in the phase diagram (Figure 6(b)), which has a distinguish "dome" structure. Parent (undoped) compound is insulating antiferromagnet and appears at low doping levels ($x < 0.025$). For undoped samples strong electronic correlation (so-called Coulomb repulsion) localizes electrons and trigger a transition to antiferromagnetic state. Neel temperature rapidly decreases with doping from 350 K at $x = 0$ to 0 K at $x = 0.025$. Increasing the level of doping, hole or electron,
samples become metallic and at \( \sim 5\% \) they become also superconductive. \( T_C \) increases with the level of doping and for optimal doping \( x \approx 0.15 \) \( T_C \) can be as high as \( \sim 100 \) K. If doping is continuing we gradually suppress the superconductivity, and the system can be described as Fermi liquid.

(a) The unit cell of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) is based on the \( \text{AXO}_3 \) perovskite structure \cite{8}.
(b) Example of phase diagram for cuprate HTSC \cite{9}.

Figure 6: Unit cell and Phase diagram.

5 Superconductivity in iron-pnictides

Until recently HTSC were the only known structures with \( T_C \) exceeding 50 K. In February 2008 Yoichi Kamihara reported on superconductivity in \( \text{LaO}_{1-x}\text{F}_x\text{FeAs} \) \((x=0.05-0.012)\) with \( T_C \sim 26\) K \cite{10}.

Transition temperature was soon pushed to even higher \( T_C \) when La was replaced with other R (rare-earth) atoms; \( R = \text{La, Ce, Nd, Sm, Pr} \). We can see (Figure 7) the progress from 23rd of February to 13th of April, when the compound \( \text{SmO}_x\text{F}_{1-x}\text{FeAs} \) \((x = 0-0.30)\) with highest \( T_C = 56 \) K was found. Since then \( T_C \) did not increase, but there is still intensive research interest in these materials and on cond-mat there is already over 1000 articles covering this field.
The excitement with this discovery was largely stimulated with some close similarities between iron-based SC and HTSC:

1) Both systems are layered in structure.

2) Parent compounds are antiferromagnets and superconductivity appears upon doping which exceeds critical value. At the same time antiferromagnetic phase is suppressed.

3) The phase diagrams are similar.

4) Both are type II superconductors.
5.1 Structure

Iron based pnictides have a typical layered tetragonal structure (Figure 8).

![Figure 8: Tetragonal structure](image)

Structure has REO layers separating FeAs layers. The REO layers act as spacer between Fe$_2$As$_2$ layers and are also charge reservoirs, similar to HTSC where first layer is superconducting second is insulating layer and third layer is hole-donating layer. In undoped samples a simple charge count predicts [LaAs]$^-$ units. The conducting (superconducting) layer is the Fe$_2$As$_2$ layer. Thus, conduction carriers are two-dimensionally confined in the Fe$_2$As$_2$ layer, causing strong interactions among the electrons. And as we can see in Figure 9 and Figure 10 the arsenic does not lie in the same plane as iron ions. Low temperature structural transitions are also very interesting. It was reported that LaOFeAs undergoes an abrupt structural phase transition below 155 K, changing the symmetry from tetragonal (space group P4/nmm) to monoclinic (spacegroup P112/n) at low temperatures, and then at $\sim 137$ K develops long range SDW-type antiferromagnetic order [12]. The REO layers can be replaced by Sr layer which results in SrFe$_2$As$_2$, or simply by Li layer (LiFeAs). In HTSCs we have CuO layers whereas in pnictides there are FeAs layers. Electrons in As(4p) are more delocalized compared to O(2p) electrons in HTSC.

The parent compound of HTSC is insulator, in pnictides the parent compound is poor conductor or sometimes also semi conducting.
5.2 Superconducting properties

In Figure 11 we show the measurements of resistivity and molar susceptibility in iron-pnictides [10]. In doped superconductive compounds $\rho$ decreases with decreasing temperature as expected for metallic compound. At $T_C = 24$ K, $\rho$ suddenly drops to 0 K indicating superconductivity.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda$ [nm]</th>
<th>$\xi$ [nm]</th>
<th>$B$ [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTSC</td>
<td>100 $\sim$ 250</td>
<td>1 $\sim$ 2</td>
<td>400</td>
</tr>
<tr>
<td>Iron-pnictides</td>
<td>180 $\sim$ 250</td>
<td>1 $\sim$ 5</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3: Penetration depth, coherence length and critical field for HTSC and iron-pnictides.

As we can see from Table 3 the superconducting parameters, for HTSC and iron-pnictides, are in the same size class. Both families of supercon-
ductors have high critical field which opens possibilities for practical use.

![Graph showing electrical resistivity and molar susceptibility versus temperature](image)

**Figure 11:** (a) Electrical resistivity ($\rho$) versus temperature (T) for undoped and La[O$_{1-x}$F$_x$]FeAs: $x = 0.04$, 0.05, 0.11 and 0.12. Inset shows expanded $\rho$-T curves for $x=0.04$, 0.05, 0.11 and 0.12. Arrows show onset transition temperatures. (b) Molar susceptibility ($\chi_{mol}$) versus T for undoped and La[O$_{1-x}$F$_x$]FeAs: $x = 0.05$. The dotted line denotes perfect diamagnetism for the sample. Inset shows expanded $\chi_{mol}$-T curves at $10^3$ times magnification of the vertical axis. An arrow shows $T_{anom}$ in part a [10].

### 5.3 Electron (band) structure

The dominated states at Fermi level come from Fe-3d atomic states, which extend roughly from -2 eV to 2 eV. At $-2.7$ eV, where the As-4p band is strongly peaked, strong mixing with Fe-3d is apparent, Figure 12. In LaOFeAs due to itinerant character of As all five Fe-d bands participate in the bonding and in the Fermi surface of compound. For typical Coulomb repulsion of Fe (4 eV) the system is found to be a bad metal. The metallic state is predicted to be strongly correlated, although this has yet to be experimentally verified. The density state is on $E_F$ which means that we are dealing with n-band conductor. The O 2p states, like the F 2p states, are essentially occupied. Replacing O with F donates one electron into the Fe 3d shell. In LaOFeAs the conducting layer is FeAs (Figure 13) while LaO layer...
plays a role of charge reservoir. The FeAs layers are conducting (highlighted in Figure 13).

![LaOFeAs, partial DOS](image)

**Figure 12:** Partial DOS states per unit cell versus energy in eV [13].

![Crystal structure of LaOFeAs](image)

**Figure 13:** Crystal structure of LaOFeAs [10].

### 5.4 Antiferromagnetic state

Magnetic structure of parent (undoped) structure was established by neutron scattering. Below $T_{SDW} = 130$ K magnetic peak starts to grow in neutron diffraction experiment (Figure 14). Measuring the intensity of magnetic peaks in neutron diffraction experiment authors [12] managed to solve the magnetic structure in LaOFeAs sample.
Figure 14: Intensity of the magnetic peak measured by neutron diffraction in LaOFeAs [12].

Simulations of neutron diffraction data show that the parent compound is long-range-ordered antiferromagnet with a simple stripe-type antiferromagnetic order within the plane that is doubled along the $c$ axis (Figure 14, top-right insight). It is clear that the lattice is distorted at 138 K, before the long-range static antiferromagnetic order sets in at $\sim 137$ K. The lattice distortion above Neel temperature is shown in the bottom-left insight in Figure 14, where a clear lattice distortion is apparent at 138 K. Magnetic structure is consistent with theoretical prediction, but the magnetic moment of 0.36$\mu_B$ per iron atom is much smaller than the predicted value of $\sim 2.3\mu_B$ per iron atom [12]. In Table 4 we compare ordered magnetic moments per ion for different compounds. The LDA predicts for all the compounds magnetic moment of $\sim 2.3\mu_B$ per iron atom and therefore by far exceeds experimental observation. The origin of this discrepancy is not yet clear, but spin fluctuations, because of the frustrated lattice, may be at the heart of this problem.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_B(Fe)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeAsO</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.36 (ND)</td>
</tr>
<tr>
<td>NdFeAsO</td>
<td>0.3 (NMR)</td>
</tr>
<tr>
<td></td>
<td>&lt;0.17 (ND)</td>
</tr>
<tr>
<td></td>
<td>0.25 (ND)</td>
</tr>
<tr>
<td></td>
<td>0.35 ($\mu$SR)</td>
</tr>
<tr>
<td>SmFeAsO</td>
<td>0.40 ($\chi$)</td>
</tr>
<tr>
<td>SrFe$_2$As$_2$</td>
<td>0.94 (ND)</td>
</tr>
<tr>
<td></td>
<td>1.0 ($\mu$SR, ND)</td>
</tr>
<tr>
<td>BeFe$_2$As$_2$</td>
<td>0.87 (ND)</td>
</tr>
<tr>
<td></td>
<td>0.40 ($\mu$SR)</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 4: Magnetic moments of RE and the ordered Fe moments. ND - neutron diffraction; $\mu$SR - muon spin relaxation; NMR - nuclear magnetic resonance.

5.5 Phase diagram of iron based superconductors

The phase diagram as a function of doping is reminiscent to copper oxides (Figure 15(a)). The superconductivity occurs when doping is around 10%. Specimen changes from poor metal to superconductor. Phase transition is not sudden, we have coexistence between poor metal phase and superconducting phase from approximately 10% to about 15%. The sensitivity of the superconductivity to the rare-earth (La, Ce, Nd, Sm, Pr) substitution is really surprising given that REO is well electronically isolated from the conducting FeAs layers, and completely different from copper oxide superconductors in which the superconductivity is only sensitive to the element substitution within the CuO$_2$ plane [12].

Phase diagram for LaO$_{1-x}$F$_x$FeAs is a little bit different (Figure 15(b)). The superconductivity occurs at approximately 4% F doping. Antiferromagnetic phase and superconducting phase are very close but not in coexistence like in SmFeAsO$_{1-x}$F$_x$. The highest critical temperature of $T_C \sim 26$ K is achieved at a F$^-$ content of $\sim 11\%$ [10].
5.6 Doping

In doping we replace $O^{2-}$ with $F^-$ in insulating $La_2O_2$ layer thus providing an extra positive charge in the insulating layer and a negative charge in the conduction layer. Superconductivity appears upon doping (Figure 11). Susceptibility for $x = 0.05$ is nearly perfect linear (Figure 16) [17]. For higher F-concentrations, this behaviour is superimposed by a susceptibility upturn in the vicinity of $T_C$ but a linear T-dependence is clearly visible at higher temperatures. It is remarkable that the static magnetic properties in $LaFeAsO_{1-x}F_x$ barely depend on the doping level $x$ while the ground state completely changes from an antiferromagnetic poor metal to a non magnetic superconductor (Figure 15(b)). When specimen is undoped we clearly see upturn of susceptibility at $\sim 140$ K (marked with arrow in Figure 16). The upturn becomes linear when doping level is $x \sim 5%$. 

Figure 15: Phase diagram for SmFeAs$_{0.1-x}$F$_x$ and La$_{1-x}$F$_x$FeAs.
Figure 16: Static susceptibility $\chi = M/B$ of LaFeAsO$_{1-x}$F$_x$, for different doping level between $0 \leq x \leq 0.125$ at $B = 1$ T. Note, that for all graphs the ordinate covers the range $\Delta \chi = 2$ emu/mol. Insets M vs. T for $B = 2$ mT [17].

6 Conclusion

Iron-pnictides have a surprisingly high critical temperature not exceeding 55 K. They stimulated research activities because of their structural similarities with copper oxides (they have antiferromagnetic phase next to superconductivity and similar phase diagram). The microscopic picture of the superconductivity in pnictides is not yet clear but it seems the antiferromagnetic fluctuations may play a vital role in electron pairing mechanism. It is hard to say anything about technical application because the research is still in progress. Iron-pnictides are relatively easy and cheap to synthesize because they are layered crystals. They have high $H_{c2}$ and are not sensitive to air. But on the other hand the arsenic is poisonous and the critical temperature is lower than 77 K which is boiling point of liquid nitrogen. So we have to use liquid helium as a refrigerant which is more expensive than liquid nitrogen.
References


