

The New Iron-Based Superconducting Materials[†]

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Abstract. Superconductivity is discussed as an astonishing property of the materials that involve many different types of applications. On fundamental level it represents a direct, macroscopic manifestation of coherent quantum mechanical behavior. The discovery of high temperature superconductors (1986) and new Iron based materials (2008) is noticed. A short introduction to the properties of the last family is given, comparing them with well established facts for cuprate perovskites. Discussion is provided about the crystal and band structure, interplay between magnetism and superconductivity, possible pairing mechanisms, anisotropy, basic critical parameters – critical temperature, critical magnetic field and critical current. Special attention is paid to superconductor-insulator quantum transition, important for non-conventional superconductors. Its deep understanding is essential for solving the problem of Cooper pairing and will help for creation of new superconducting materials. A brief presentation of the first results on synthesis of iron based superconductors at the Institute of Solid State Physics is presented.

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1 Introduction

The discovery of high-temperature superconductivity (HTSC) in copper oxides more than 20 years ago stirred up profound interest and has led to the publication of thousands of experimental and theoretical articles. The electron-phonon coupling as proposed in BCS theory is not sufficient to induce superconductivity at such high temperatures. In these cuprate superconducting materials, superconductivity develops from electronically doping an antiferromagnetic Mott insulating phase with carriers. It is thus hoped that one may eventually understand the high-T_c superconductivity in terms of the interplay between magnetism and superconductivity.

Research on high-T_c superconductivity turned in a new direction in the year 2008 with the discovery of iron-pnictide superconductors. Hosono's group re-

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ported of superconductivity in $\text{LaFeAsO}_{1-x}\text{F}_x$ (labelled 1111, based on the elemental ratios in the chemical formula of the parent material) with $T_c = 26$ K [1]. The T_c was soon raised to 43 K, either by replacing La with Sm ($\text{SmFeAsO}_{1-x}\text{F}_x$) [2], or by applying pressure [3]. Several 1111 superconductors with $T_c > 50$ K have been successively reported, and the current record is 56 K in $\text{Gd}_{1-x}\text{Th}_x\text{FeAsO}$ [4]. In the ensuing months, many other superconducting Fe-pnictides have been discovered. They are grouped into five homologous series, 1111 (RFeAs with R = rare-earth; AeFFeAs with Ae = alkaline earth), 122 (AeFe_2As_2 ; AFe_2As_2 with A = alkaline), 111 (AFeAs), 11 (FeSe) and the $\text{Sr}_2\text{MO}_3\text{FePn}$, M = Sc, V, Cr (21311) family. Similar to the cuprates a new class of high temperature superconductors have been discovered, the so-called iron pnictides (FePn, where Pn = As or P) and iron chalcogenides (FeCh, where Ch = S, Se and Te).

Very interesting, aspect of Fe-containing superconductors from a basic physics point of view is the superconducting pairing mechanism. Superconductivity and magnetism were considered as exclusive phenomena. According to BCS theory superconductivity results from the pairing of electrons with opposite spin, while in magnetism electron spins are ordered and fixed in space. An important question is whether the magnetic and superconducting properties originate from the same orbital electrons. According to current understanding in Fe-based superconductors magnetic and superconducting phases coexist. They may coexist in different areas displaying phase separation or in unique phase on atomic (nano-) scale with electronic phase separation characteristics.

2 Structural Properties

The structure is crucial in any attempt to understand the superconductivity at any new class of superconductors. For example, the orthorhombic crystal structure with the higher oxygen content, (respectively carriers) than tetragonal is decisive for superconductivity in cuprate superconductors.

The Fe-based superconductors are characterized by a simple crystalline structure: iron pnictogen (P, As) or chalcogen (S, Se, Te) superconducting active layers, separated by spacer layers of rare earth oxide/fluoride (LaO or SrF) Figure 1(a); alkaline earth (Ba) – 1(b); alkali (Li) – 3(d) or simply stacked together (1(c)), as in FeSe which is the simplest crystalline structure formed of only two elements.

The fifth structure with FePn planes from this superconducting set of materials is the so-called 21311 (sometimes called the 42622) structure. This structure can be visualized as layers of $122 \text{ SrFe}_2\text{P}_2$ alternating with perovskite $\text{Sr}_3\text{Sc}_2\text{O}_6$ layers. Intercalation of further layers of atoms between the FeAs layers to try to increase T_c by expanding the c-axis has so far resulted in T_c up to 47 K. Thus, all of the discovered FePn/Ch superconductors are tetragonal with planes of tetrahedra of

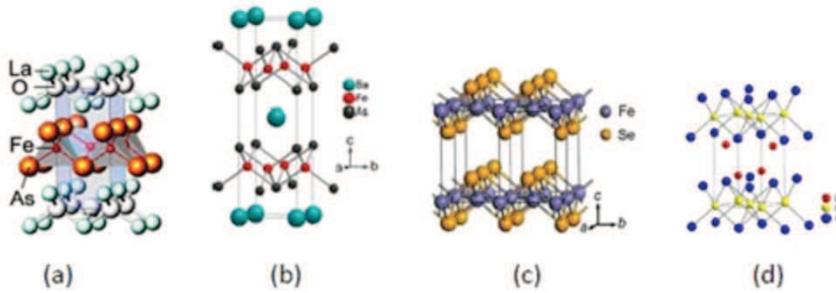


Figure 1: The lattice structure of 1111 LaFeAsO (a); 122 BaFeAs (b); 11 FeSe (c) and 111 LiFeAs (d).

Fe and either As or P (pnictogens) or S, Se or Te (chalcogenides).

The other important similarity (after the 2D layers) is a spin density wave (SDW) antiferromagnetism [5]. It is reported for the undoped parent compound LaFeAsO with $T_{\text{SDW}} = 137$ K for undoped BaFe₂As₂ with $T_{\text{SDW}} = 140$ K, as well as a tetragonal-orthorhombic structural distortion at the same temperature. Finally the 11 structure FeSe_{1-x}, $T_c = 8$ K, shows a structural transition (just like the 1111 and 122 structures, tetragonal to orthorhombic) at 90 K with no magnetic transition, while FeSe_xTe_{1-x}, $T_c = 15$ K, has both a structural (tetragonal to monoclinic) and magnetic transition (both at 72 K for $x = 0$). Only LiFeAs, shows bulk superconductivity at $T_c = 18$ K but has neither a magnetic nor a structural transition, although there are very strong magnetic fluctuations. Thus the parent compounds of iron pnictides and iron chalcogenides exhibit SDW or antiferromagnetic order. All these indicate that the superconductivity in Fe-based superconductors is close to magnetism and spin fluctuations may be important for pairing mechanism.

A direct correlation of superconductivity to spin fluctuation is the pressure effect. T_c was significantly increased under pressure in FeSe (from 8 K at zero pressure up to 37 K at 7 GPa [6]). Thus it is evidently not necessary to dope additional carriers into the parent compounds to induce superconductivity, but only to suppress the crystallographic and long-range-antiferromagnetic transitions.

3 Band Structure

Many band structure calculations have been carried out for the Fe-based high- T_c superconductors. For a transition metal cation at the center of a tetrahedron of electronegative anions, due to crystalline electric field effects one nominally expects the five d -orbitals to split into a low energy set of two so-called e_g orbitals and a set of three t_{2g} orbitals at higher energy. In oxides, this splitting is clearly seen. However, in the FeAs-type materials all five d -orbitals are at

about the same energy, and hence the bands formed from them overlap near the Fermi energy to a large extent. Furthermore, the electronic density of states at the Fermi energy is primarily derived from the *Fe* 3d orbitals, and the *As* 4p-orbitals do not contribute much. This indicates that direct hopping of electrons from *Fe* atom to *Fe* atom is the main mechanism for metallic conduction, rather than hopping from *Fe* to *As* to *Fe* [7].

A critically important feature of the *Fe*-based superconductors is that they are semimetals. A semimetal is a material having finite conductivity as the absolute temperature T approaches zero Kelvins. To explain the difference between two-dimensional semiconductor and semimetal a sketch of their band structure is shown in Figure 2. By definition, the band structure of a material is the set of dependencies of the energies of itinerant (movable) current carriers as a function of their momenta k .

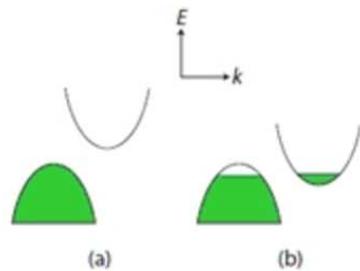


Figure 2: (a) A band gap semiconductor with a filled lower valence band and an empty upper conduction band at temperature $T = 0$, the material is an insulator. (b) A semimetal. Here, the valence and conduction bands overlap slightly in energy and some electrons from the valence band spill over to the conduction band until the energies of the highest occupied electron states in each band become the same (the Fermi energy).

If the material is ‘doped’ with excess electrons or holes, then the electron and hole concentrations are no longer the same. In the absence of electron correlation effects the material is metallic at $T = 0$ because there are either electrons in the conduction band or holes in the valence band, respectively. There is no longer an energy gap. Therefore electrons ‘spill over’ from filled valence band into the conduction band until the highest energy occupied state in each band (the Fermi energy) is the same. This results in small electron and hole ‘pockets’ of current carriers. The existence of the electron and hole pockets allows a new type of superconducting pairing to occur, known as s_{\pm} pairing. This pairing is specific to the type of semimetallic electronic structure and the superconducting order parameter has opposite signs on the electron and hole pockets.

4 Critical Parameters

As it has been pointed yet the maximal T_c obtained for Fe-based superconductors is ~ 56 K which means that it is not possible to use the liquid nitrogen as cooling agent.

Application of an external magnetic field may destroy the Cooper pairs in the following two ways: i) the orbital pair breaking due to the Lorentz force acting via the charge on the paired electrons, known as the orbital limit and (ii) the Pauli paramagnetic pair breaking as a result of the Zeeman effect which aligns the spins of two electrons with the applied field, called the Pauli paramagnetic limit. In conventional superconductors, the upper critical field is mainly restricted by the orbital pair-breaking mechanism. However, spin paramagnetic effect may become dominant for pair breaking in unconventional superconductors, e.g., the heavy fermion superconductors and the organic superconductors. Estimations of $\mu_0 H_{c2}(0)$ from its initial slopes near T_c using the Werthamer-Helfand-Hohenberg model (WHH) gives a value as high as 100–300 T. The experimental investigations confirmed in some extent these predictions. Extrapolation of $\mu_0 H_{c2}(T_c)$ to zero temperature for single crystalline $\text{NdFeAsO}_{0.82}\text{F}_{0.18}$ ($T_c = 49$ K) and $\text{Ba}_{0.55}\text{K}_{0.45}\text{Fe}_2\text{As}_2$ ($T_c = 30$ K) gives $\mu_0 H_{c2}^{H||ab}(0 \text{ K}) = 304$ T (and 110 T) and for $\mu_0 H_{c2}^{H||c}(0 \text{ K}) = 70$ T (and 75 T), respectively [8]. $\text{Fe}_{1.11}\text{Te}_{0.6}\text{Se}_{0.4}$ also possesses a large upper critical field of 45 T at zero temperature in spite of its relatively low superconducting transition temperature ($T_c \sim 14$ K). Such large and isotropic upper critical field in combination with large critical current weakly suppressed in magnetic field, are useful for potential applications.

5 Superconductor-Insulator Transition

For many classical superconductors destruction of superconductivity leads to restoration of metallic conduction. However in the last 30 years it was realized that in some electronic systems destruction of superconductivity can lead to obtaining of an insulator. Classical superconductors have high electronic concentration and high coherence length of Cooper pairs ($\xi \sim 10^{-4}$ cm), when compared with the mean distance between the pairs ($s \sim 10^{-6}$ cm). After discovery of HTSC it was shown that in systems with smaller electronic concentration ($\sim 10^{19} \text{ cm}^{-3}$) and $\xi \leq s$ the superconductor-insulator quantum transition is possible. These materials are not classical BCS superconductors. For them a new model of superconductivity (Bose-Einstein condensation) has been proposed. According to this model, Cooper pairs exist on both sides of superconducting transition, but they are correlated only below T_c . It is supposed that better understanding of superconductor-insulator transition will help for establishing of mechanism of superconductivity in HTSC.

6 Obtaining and Investigations of Fe-Based Superconductors

Since 2012 polycrystalline samples FeSe and FeSeTe are obtained and investigated in Low temperature Physics Lab at the Institute of Solid State Physics, BAS. The T_c of 8 K and 14 K have been observed for both systems, respectively. We have some progress in technology for preparation of good samples as well in improvement of inter-grain connections and AC magnetic susceptibility high harmonics analysis.

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