Superconductivity in Fe-Chalcogenide

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May 12, 2018

Abstract

Shortly after the discovery of iron-based superconductor(FeSC) in early 2008, iron-chalcogenide FeX (X=Se,Te,S) emerged as a promising group of compounds for studying the mechanism of iron-based superconductivity. In this term paper, the physical and chemical properties of iron-chalcogenide(FeCh) superconductor are reviewed, progresses in the study of its pairing mechanism are discussed and some of the recent experimental results are summarized.

1   Introduction

Iron-based superconductor(FeSC) is a relatively new type of unconventional superconductor that was first discovered in 2008 by the research group lead by Hideo Hosono in Japan[1]. Shortly after, Hsu et al. reported the discovery of a superconducting phase in the PbO(lead oxide)-type alpha-FeSe compound with T_c=8K[2]. This led to an extensive study of superconductivity in iron-chalcogenides(FeCh). FeCh has several desirable features that contribute to its popularity. Many FeCh superconductors have very simple crystal structures, but exhibit complex phase diagram that is very sensitive to small variation in composition or pressure, enabling exploration of a wide range of electronic and magnetic behavior. Owing to the simplicity of its structure, FeCh is preferable in the study of pairing mechanism of FeSCs. FeCh also has high potential for applications. In Hsu's 2008 paper, they reported an upper critical field of 16.3T at zero temperature for FeSe, which makes iron-chalcogenides strong candidate for high magnetic field applications[2] such as superconducting magnet.

2   Physical and Chemical Properties of FeCh

2.1   FeSe

Iron selenide(FeSe) compound has the simplest crystal structure of all FeCh, despite a complicated phase diagram. The superconducting phase is the PbO-type tetragonal phase (space group P4/nmm) as shown in Figure 1(a)[2]. The black rectangles indicate the size of the unit cells. Selenium anions are layered in between two planar layers of iron, so the compound is quasi two-dimensional. Like many other FeCh, FeSe is a Van der Waals material, which means that the compound are held together by Van der Waals forces between adjacent layers of selenium without real chemical bonding.

Figure 1(b) shows the resistivity versus temperature curve of bulk $FeSe_{0.88}$. The transition to superconducting state occurs around T=8K. The left inset shows the dependence of critical temperature on external magnetic field. The transition width for all external field is rather broad. The right inset shows the upper critical field dependence of temperature, where the upper critical field is proportional to the temperature squared. An upper critical field of 16.3T at zero temperature is predicted from this data, giving a coherence length of about 4.5nm using Ginzburg-Landau theory[2].

The ratio between iron and selenide plays crucial rule in affecting the critical temperature. Superconducting FeSe compound is slightly selenium deficient. At atmosphere pressure a critical temperature of 9K can be reached with bulk $Fe_{1.1}Se$, but it quickly drops to 5K for bulk $Fe_{1.2}Se$. Superconductivity is completely suppressed when the ratio exceeds 1.3[3].

Pressure is also found to have strong effects on critical temperature[4]. An

(a) PbO-type FeSe tetragonal lattice   (b) FeSe Resistivity vs. T curve
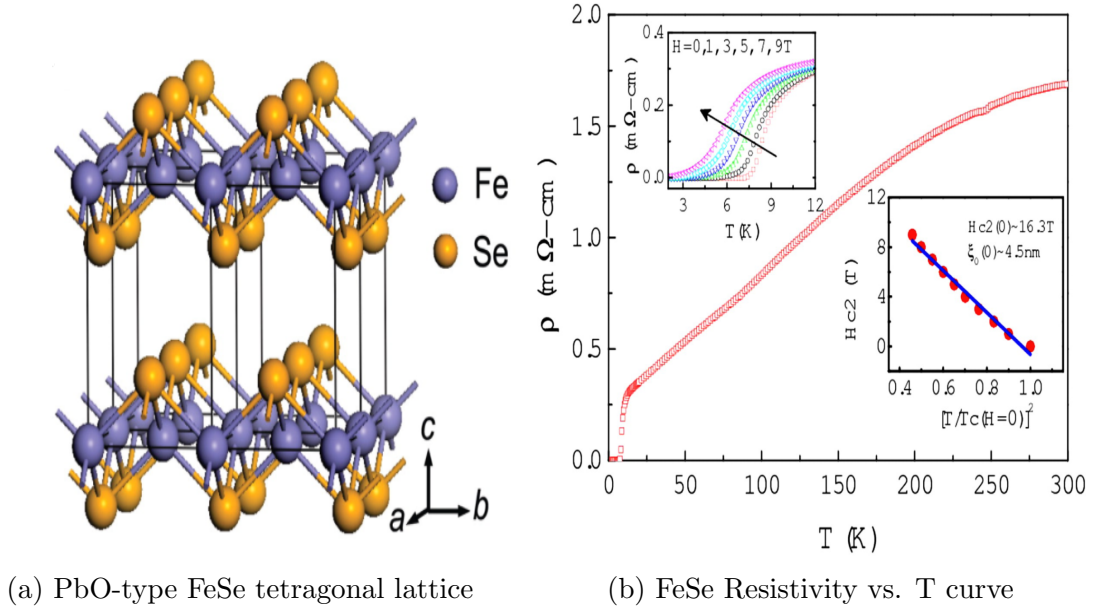
Figure 1

increase in pressure changes the crystal structure of FeSe, which is reflected in the measurement of anion height, the planar distance between iron and selenium layers. Figure 2 shows the effects of varying pressure on T_c. It is noted that in figure 2(b), the data for FeSe only falls on the solid red fitting curve for pressure larger than 2 GPa. This corresponds to big jumps in critical temperature and anion height around 2 GPa as shown in figure 2(a). Above 4 GPa, onset T_c reaches around 37K.

2.2   FeTe and FeTeSe

Iron telluride(FeTe) has similar crystal structure to that of FeSe, but it has very different physical properties. Compared to FeSe, FeTe has substantially more iron than chalcogen anions, reaching up to 25 percents. Bulk FeTe does not superconduct, but FeTe thin film on MgO is found to be superconducting under tensile stress[5]. Figure 3 shows the resistivity and magnetic susceptibility dependence of FeTe thin film on temperature. It is interesting that the critical temperature is much less affected by external magnetic field than in the case of FeSe. The zero temperature upper critical field is predicted to be around 123.0T for FeTe thin film on SrTi0 $_3$ substrate, which is significantly higher than that of FeSe.

Due to the similarity of the crystal structures of FeSe and FeTe, partial chemical substitution of tellurium by selenium in FeTe is possible without significantly changing the lattice structure. The resulting compound is called $FeTe_{1-x}Se_x$. Bulk FeTe is not superconducting due to an anti-ferromagnetic transition that happens around the Neel temperature T_N of 70K, but the partial substitution of Te by Se suppresses the transition and induces superconductivity. As mentioned before, be-
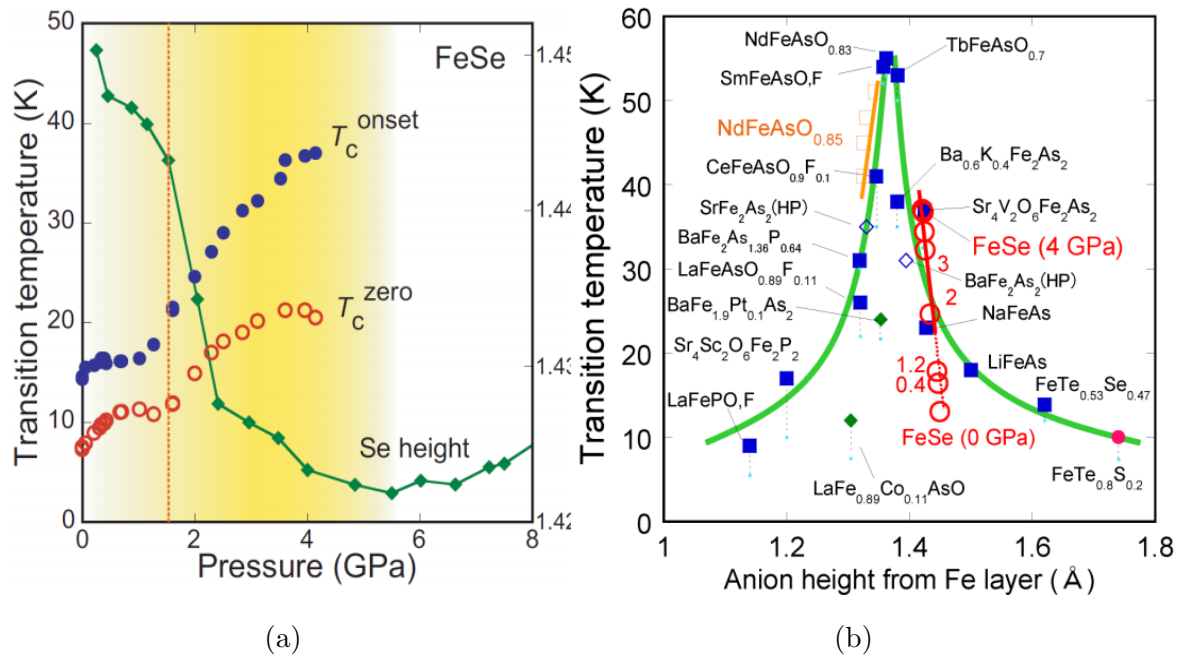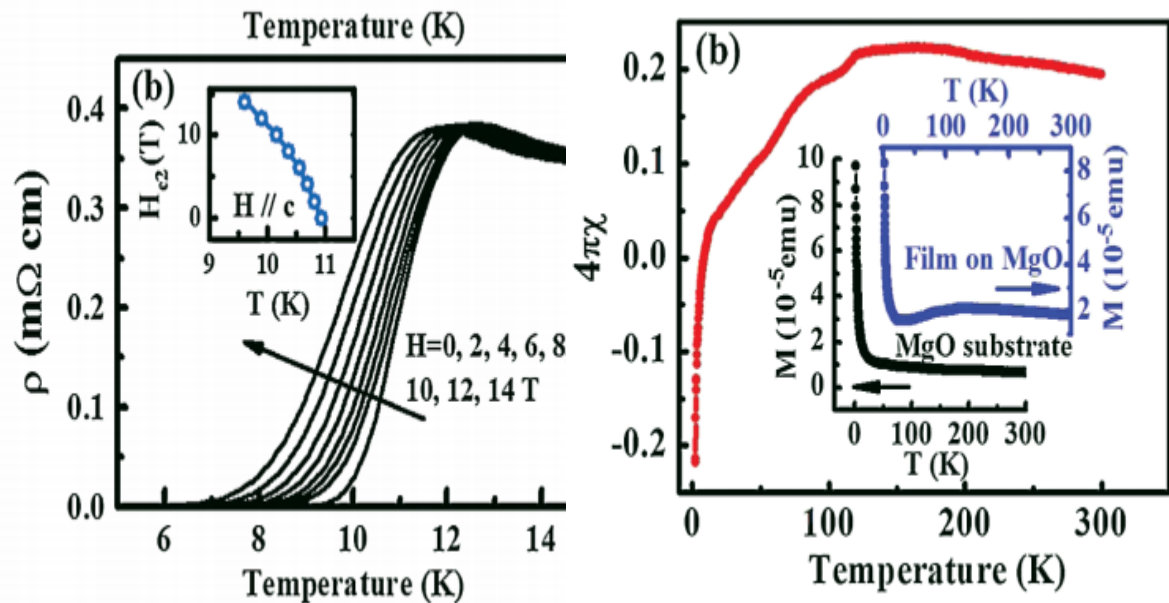
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(a)   (b)

Figure 2: Pressure and anion height dependence of T_c in FeSe[4]

(a) FeTe thin film on $SrTiO_3$ substrate   (b) FeTe thin film on MgO substrate

Figure 3: Reference from [5]

havior of FeCh compounds is very sensitive to the actual chemical composition. Y. Mizuguchi et al. reported critical temperature and magnetic susceptibility measurement on $FeTe_{1-x}Se_x$ compounds with different value of x[6].

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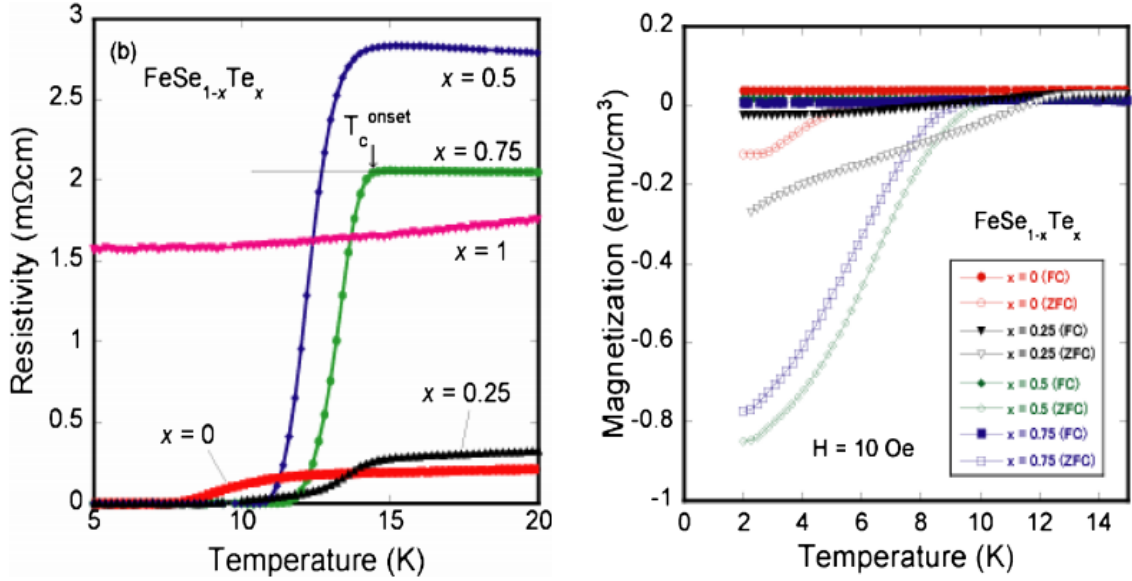
(a) Temperature dependence of resistivity of FeSe$_{1-x}$Te$_x$

(b) Temperature dependence of magnetization of FeSe$_{1-x}$Te$_x$

Figure 4: Reference from [6]

Part of their results is summarized in figure 4. We can see that for x=1, which corresponds to FeTe, there is no superconducting transition at all. Increasing concentration of selenium induces superconductivity and increase T_c. FeSe$_{0.5}$Te$_{0.5}$ and FeSe$_{0.25}$Te$_{0.75}$ have relatively high onset transition temperature and sharp transition. FeSe$_{0.5}$Te$_{0.5}$ also has the highest magnetization among all the composition studied. Many recent studies of FeSe$_{1-x}$Te$_x$ have been using FeSe$_{0.5}$Te$_{0.5}$ as parent compound.

Extensive research has gone into the physical and chemical properties of FeCh superconductors. Up to date, numerous FeCh samples of 11(like Fese), 111(like FeSeTe), 122(like AFe$_2$Se$_2$, where A is an Alkaline metal) and other types are fabricated and studied. Due to the length constraint on this term paper, only some of the most basic compounds are introduced here.

3 Pairing Mechanism of Iron-based Superconductors

Like the cuprates, FeSCs are unconventional due to their pairing mechanisms. In conventional superconductors, as explained by the BCS theory, superconductivity is achieved by electrons pairing together forming Cooper pairs coupled by electron-phonon interaction. The pairing of electrons open a gap on the Fermi surface, which allows the condensation of Cooper pairs. This is very similar to superfluidity

in Helium III. But in cuprates and FeSCs, electron-phonon interaction is found to be insufficient to explain the pairing mechanism. There are building evidences that electron-electron interaction also plays important rule in these unconventional superconductors.

3.1 Pairing Symmetry

The pairing symmetry for conventional BCS superconductor is s-wave symmetry and the superconducting gap is isotropic. It is widely believed now that cuprate superconductor has $d_{x^2-y^2}$ pairing symmetry. The pairing symmetry of FeSC, however, has been debated for quite a long time. According to Density Functional Theory(DFT) calculations and experiments, it is found that FeSC has multi-band structure and has several disconnected Fermi Surfaces(FS). For system with multiple FS, electrons can scatter from one FS to another, with a change of sign in order parameter[7]. A popular theory is that the pairing symmetry is the $s_\pm$ state or probably its variations[8], which are shown in figure 5.
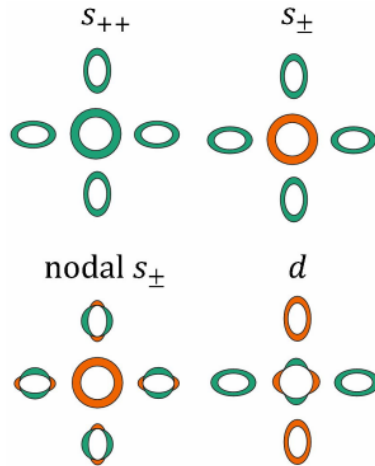

Figure 5: Order parameter for different symmetries[8]

The FS in the center is hole-like, which means that the filled states are outside of the surface, and those to the side are electron-like, so the filled states are inside the surface. The color indicates the sign of order parameter, and the width indicates the magnitude. For $S_\pm$ symmetry, the order parameter changes sign as we go from a hole-like FS to an electron-like FS. Sometimes nodes will appear in the electron-like FS, like in the case of nodal $s_\pm$ symmetry. The order parameter changes sign within a single FS. Notice that these s-wave states are symmetric under $90°$ rotations (cyclic group C_4), but the d-wave shown is not.

A.Chubukov argued that pairing symmetry is dependent on doping of FeSCs[9]. For weakly or moderately electron-doped and hole-doped samples, $s_\pm$ and $d_{x^2-y^2}$ pairing are nearly degenerate. The pairing force is the electron-hole interaction

enhanced by spin fluctuation. For strongly electron-doped sample, the pairing force is nodeless d-wave direct attraction between electron-Like FS. For strongly hole-doped sample, when only the hole-like FS remains, the symmetry is nodal d-wave attraction within hole-like FS at the first BZ corners and interaction between two hole-like FS centered at the center of the first BZ. But of course no decisive evidence has been found to test all his theories.

FeCh has received great attention in the research of FeSC pairing symmetry because the theory for $S_\pm$ pairing assumes the existence of both electron and hole like FS. Recent experiments done on Alkali-intercalated FeSe(usually AFe_2Se_2 where A= K, Rb, Cs) or single layer FeSe grown on $SrTiO_3$ substrate suggest possibility for more different pairing symmetries, because of the absence of hole-like FS in the center of the first Brillouin Zone(BZ)[10]. This raise the question whether the pairing symmetry in FeSCs is universal or dependent on materials.

3.2 Pairing Mechanism

Controversies also remain in the determination of the pairing mechanism of FeSC. There are several competing pairing theories.

3.2.1 Spin Fluctuation

The $S_\pm$ pairing symmetry is predicted by combining a three-orbital or five-orbital Fe-only tight binding model with spin fluctuation interaction, and the results qualitatively agree with experiments. Almost all calculations of this type is done with a multiband Hubbard Hamiltonian including a multiband tight binding kinetic energy, Hubbard interaction, inter-orbital Hubbard interaction, exchange and "pair hopping interaction"[10]. Efforts have been made to calculate the tight binding kinetic energy term from DFT calculation, assuming that the coulomb interactions are localized, and determine the various interaction terms based on first principle calculations.

3.2.2 Orbital(Charge) Fluctuation

Apart from the spin degree of freedom, orbital degree of freedom is also taken into account by many theories. In the spin fluctuation calculated mentioned above, charge fluctuation is considered to be dominated by spin fluctuation. The initial study in this direction focused on possibility of enhancing inter-orbital Coulomb interaction. It is shown that if the enhancement is possible, then the pairing will produce a s_{++} symmetry[10]. But it is more likely that the pairing mechanism is an interplay of the two fluctuations mentioned, as the degree of these fluctuations is not universal in all FeSCs.

3.2.3 "Strong Coupling"

Strong coupling theory is based on the J_1-J_2 Heisenberg Model. Its Hamiltonian not only includes interaction between spins of nearest neighbors, but that of next nearest neighbor and so on, assuming that the coupling is "strong". The interaction is then decoupled in the pairing channel in mean field theory, such that the nearest neighbor interaction leads to s_- and $d_{x^2-y^2}$ pairing harmonics, and the next nearest neighbor term leads to s_- and d_{xy} pairing harmonics. It is found that if the interaction with the next nearest neighbor is somehow relatively stronger than with the nearest neighbor, a nodeless $s_\pm$ state is obtained[10].

To conclude this section, the exact pairing mechanism of FeSC is still not known. Recent experiments have come up with plenty of counter examples that contradict former theories. Based on literatures up to date, it is highly likely that the pairing is based on several mechanisms that are not universal among all FeSCs. An improvement in sample quality and measurement techniques may help us better understand and resolve this issue in the future.

4   Recent Experimental progresses

Techniques of fabricating and measuring samples have undergone rapid development in the past few decades. In sample growing, Molecular Beam Epitaxy(MBE) and Pulse Laser Deposition(PLD) are widely used. The growth of thin films, or even monolayer samples are possible and well documented. Reducing samples from bulk down to several layers of atoms reveals many new phases that are not seen in bulk form, and in many cases increase T_c significantly. JianFeng Ge et al. reported a T_c of nearly 80K in FeSe thin film grown on Nb-doped $SiTrO_3$ in 2014, which is ten times higher than the critical temperature of bulk FeSe when it was first discovered in 2008 and also higher than the record value of T_c=56K for all bulk FeSCs. They claimed that this FeSe/STO combination can have T_c up to 100K with in-situ measurement[11]. Part of their results is summarized in figure 6. Figure 6(a) is the resistivity versus temperature graph, and figure 6(b) is the upper critical field versus temperature graph. The superconducting transition is much sharper than the bulk samples shown earlier in this paper. A very high (about 116T) zero temperature upper critical field is also achieved.

Recent research by M.Molatta et al. addressed inhomogeneity issue in stoichiometry and texture of $FeSe_{1-x}Te_x$ thin film on different substrates[12]. They proposed the implementation of a so called seed layer of semiconducting $FeSe_{1-x}Te_x$ that allows for homoepitaxial growth of thin film. Before their research, others had shown that a buffer layer of iron is able to improve lattice matching between sample and substrate and reduce defects[13]. Molatta argued that this conductive layer of iron displays detrimental ferromagnetism that is not desirable. They showed that using the seed layer they were able to produce smoother $FeSe_{1-x}Te_x$ thin film at a much lower temperature than before (240° compared to 300°). The seed layer

also improves lattice matching, making the growth of $FeSe_{1-x}Te_x$ on MgO, which is one of the most favorable substrates for thin film growth for many other FeSCs, possible because it overcomes a huge lattice mismatch between $FeSe_{1-x}Te_x$ and MgO of about 11 percent. They demonstrated that this implementation allows improved control and reproducibility of structural properties of $FeSe_{1-x}Te_x$ thin films and may be helpful for fabrication of other superconductors on MgO.

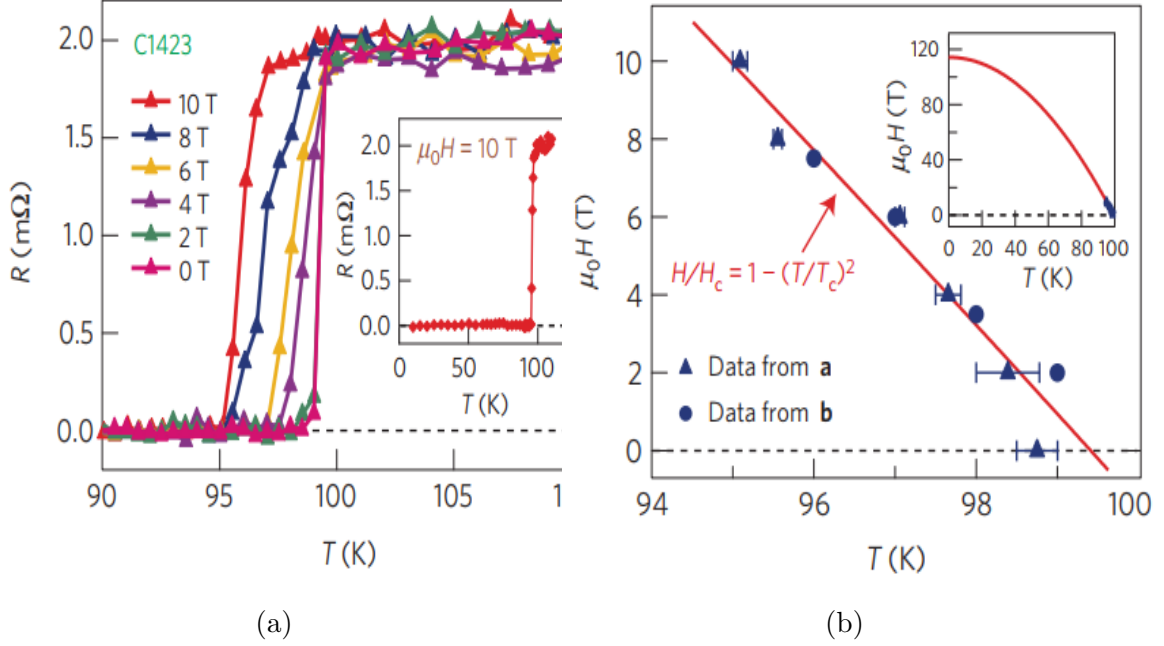(a)   (b)

Figure 6: Reference from [11]

5   Conclusion

Iron-chalcogenide is a rich subfield in iron-based superconductors that has been intensively study, but many questions remain unanswered. This term paper represents an attempt to understand the subject briefly. The physical and chemical properties of simple FeCh are introduced, followed by a discussion of the study of possible pairing mechanisms. The exact pairing mechanism is under heated debate without decisive evidences supporting a particular theory. The most important question of whether there exists an universal pairing mechanism still begs answers. At the meantime, with the help of advancing experimental techniques like MBE, PLD, ARPES and its variations, Scanning Tunneling Microscope(STM) and many others, we can now fabricate samples with great precision in dimension and composition, and measure their properties from many different angles. Hopefully more of the physics of iron-chalcogenide and iron-based conductors will be understand soon and we can benefit from the applications that it derives.

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