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TOPICAL REVIEW

Iron chalcogenide superconductors at high magnetic fields

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Abstract
Iron chalcogenide superconductors have become one of the most investigated superconducting materials in recent years due to high upper critical fields, competing interactions and complex electronic and magnetic phase diagrams. The structural complexity, defects and atomic site occupancies significantly affect the normal and superconducting states in these compounds. In this work we review the vortex behavior, critical current density and high magnetic field pair-breaking mechanism in iron chalcogenide superconductors. We also point to relevant structural features and normal-state properties.

Keywords: iron chalcogenide superconductors, upper critical fields, vortex physics, critical current density

1. Introduction

The discovery of superconductivity in La(O,F)FeAs with superconducting transition temperature $T_c = 26$ K [1] stimulated intensive research on related materials. This resulted in the discovery of several families of iron-based superconductors with the highest $T_c = 56$ K [1–23], including REOFepn (RE = rareearth; Pn = P or As, FePn-1111 type) [1–7], AFe$_2$As$_2$ (A = alkaline or alkaline-earth metal, FeAs-122 type) [8–10], AFeAs (FeAs-111 type) [11, 12], (Sr$_2$M$_2$O$_6$)(Fe$_2$Pn$_2$) (M = Sc, Ti or V, FePn-42622 type) [13, 14], FeCh (Ch = S, Se, Te, FeCh-11 type) [15–17] and A$_2$Fe$_{2-x}$Se$_2$ (AFeCh-122 type) [18–23].

The crystal structure of FeCh and AFeCh-122 systems features a square-planar lattice of Fe with tetrahedral coordination, which is the common ingredient found in all iron-based superconductors, but they also have some distinctive characteristics. For example, FeCh-11 type materials have a rather simple crystal structure without the charge reservoir layer. FeSe exhibits a significant pressure effect [24]; under external pressure, the $T_c$ can be increased from 8 to 37 K and the $dT_c/dP$ can reach 9.1 K GPa$^{-1}$, the highest increase in all iron-based superconductors. FeTe,Se and Fe(Se,S) contain strongly magnetic excess Fe in Fe(2) site that provides local moments and tunes details of magnetic structure depending upon the amount of excess Fe [25, 26]. On the other hand, in AFeCh-122 materials the hole Fermi surfaces (FSs) are absent [27, 28], which is different from other iron-based superconductors where both electron and hole FSs are present [29], suggesting pairing symmetry other than $s\pm$ [30]. There are also vacancies in the Fe plane that order at $T = 578$ K resulting in long-range antiferromagnetic (AFM) order at $T_N = 559$ K [31]. Finally, one of the most distinctive features in AFeCh-122 is the proximity of semiconducting state [23], which is magnetic but is spatially separated and coexists with superconducting regions on the 10–100 nm length scale [32–38]. This is different from iron pnictides where superconductivity emerges when the spin density wave (SDW) state is suppressed [39].

On the other hand, because of large upper critical fields $\mu_0H_{c2}$ and small lower critical fields, iron-based...
superconductors exhibit rich vortex phenomena in the mixed state and exotic temperature dependences of $\mu_0 H_c(2)$. There are also some promising technical application perspectives due to high $T_c$ and large $\mu_0 H_c$. The distinctive features of iron chalcogenides will lead to the pronounced differences of the superconducting properties in magnetic fields when compared to pnictides, such as the different contributions of multiband and spin paramagnetic effects which will determine the temperature dependence of the $\mu_0 H_c(T)$, the different strengths of vortex thermal fluctuations in mixed state and the different behaviors of critical current density $J_c$ in magnetic fields.

In this paper, we review the superconducting properties of iron chalcogenide superconductors in high magnetic fields, while comparing these properties with those of iron pnictide superconductors. In section 2, we address vortex physics, especially thermally activated flux flow. Section 3 describes the $J_c$, and in section 4, we describe the important features of $\mu_0 H_c$ and compare $\mu_0 H_c$ in iron pnictide and iron chalcogenide superconductors. Finally, in section 5, we summarize the main results we discussed and outline general perspectives of this field.

2. Vortex physics in iron chalcogenide superconductors

Iron-based superconductors are extreme type-II superconductors with $\kappa \sim 100$ and a large range of magnetic field penetration in the mixed state of $\mu_0 H-T$ phase diagram. Hence, rich vortex physics is expected in all iron-based superconductors. In the mixed state the thermal fluctuation effects on the vortex behavior can be quantified by the Ginzburg number $G_i$

$$G_i = \frac{1}{2} \left( \frac{k_B T_c}{\mu_0 H_c^2 \xi_{ab}(0) \xi_c(0)} \right)^2,$$

where $k_B$ is Boltzmann constant, $\mu_0$ is vacuum permeability, $\mu_0 H_c(0) = \phi_0 / 2\sqrt{2}\pi \lambda_{ab}(0) \xi_{ab}(0)$ is the thermodynamic critical field ($\phi_0$ is magnetic flux quantum), $\lambda_{ab}(0)$ is the London penetration depth in the $ab$ plane, and $\xi_{ab}(0)$ and $\xi_c(0)$ are the coherence lengths in the $ab$ plane and $c$-axis, at $T = 0$ K, respectively. Here we assume $\xi_0(0) = \xi_b(0) = \xi_{ab}(0)$, which is consistent with the tetragonal lattice symmetry of iron-based superconductors. The $G_i$ is basically the squared ratio of the thermal energy to the condensation energy in the volume occupied by the Cooper pair [40]; it can be rewritten as [40]

$$G_i \propto \gamma_m^{4/3} m^4 T_c^{-4} n^{-8/3},$$

where $\gamma_m$ is the mass anisotropy in a uniaxial crystal, $\gamma_m = m_c / m_{ab} = (\xi_{ab}/\xi_c)^2 = (H_{c2,ab}/H_{c2,c})^2$, and $m$ is the effective mass and $n$ is carrier density. The $G_i$ can be increased strongly if (i) $T_c$ increases, (ii) effective mass increases, (iii) mass anisotropy increases or (iv) carrier density decreases. In the layered cuprate oxide superconductors vortex behavior can be affected dramatically by thermal fluctuation ($G_i \sim 10^{-3} - 1$) because of high $T_c$ and large $\gamma_m$ when compared to conventional Bardeen–Cooper–Schrieffer (BCS) superconductors where vortex thermal fluctuation is negligible ($G_i \sim 10^{-10} - 10^{-6}$) [40]. In iron-based superconductors, thermal fluctuation effects ($G_i \sim 10^{-4} - 10^{-2}$) also influence vortex properties [40]. Some iron-based superconductors exhibit significant vortex fluctuations similar to those in the cuprates with smallest anisotropy, such as YBa$_2$Cu$_3$O$_{7-x}$ (YBCO), despite smaller $T_c$ and $\gamma_m$. Relatively large thermal fluctuation effects may be related to the low $n$ and large $m$ [41–43]. In FeCh-11 superconductors, $T_c$ is smaller at ambient pressure as compared to FeAs-122 materials but the $G_i$ ($\sim 10^{-2}$) is larger than the latter one ($G_i \sim 10^{-4}$) [40], which could be ascribed to the significant mass enhancement [41]. Therefore, thermally activated vortex dynamics is expected even at low temperatures.

2.1. Thermally activated flux flow

Thermal fluctuations in FeCh-11 superconductors can result in the thermally activated flux flow (TAFF) behavior where the vortex bundles hop between neighboring pinning centers. According to the TAFF theory, the resistivity in TAFF region can be expressed as [44–46]

$$\rho = (2\rho_0 L_B/J) \exp(-J_B V L / T) \sinh(J B V L / T),$$

(3)

where $\rho_0$ is an attempt frequency for a flux bundle hopping, $L$ is the hopping distance, $B$ is the magnetic induction, $J$ is the applied current density, $J_0$ is the critical current density in the absence of flux creep, $V$ is the bundle volume and $T$ is the temperature. If $J$ is small enough and $J B V L / T \ll 1$, we obtain

$$\rho = (2 \rho_0 U / T) \exp(-U / T) = \rho_0 f \exp(-U / T),$$

(4)

where $U = J_0 B V L$ is the thermal activation energy and $\rho_0 = L B / J_0$, which is usually considered to be temperature independent. For cuprate superconductors, the prefactor $2 \rho_0 U / T$ is usually assumed as a constant $\rho_0 f$ [45], therefore, $\ln \rho(T, \mu_0 H) = \ln \rho_0 f - U(T, \mu_0 H) / T$. On the other hand, according to the condensation model [46], $U(T, \mu_0 H) = (\mu_0 H_c(i))^2 \xi^2 \Phi_0(t)$, where $\mu_0 H_c$ is the thermodynamic critical field, $\xi$ is the coherence length, $t = T / T_c$, and $n$ depends on the dimensionality of the vortex system with the range from 0 to 3. Since $\mu_0 H_c \propto 1 - t$, and $\xi \propto (1 - t)^{-1/2}$ near $T_c$ [47], it is obtained that $U(T, \mu_0 H) = U_0(\mu_0 H)(1 - t)^n$, where $q = 2 - n / 2$. It is generally assumed that $U(T, \mu_0 H) = U_0(\mu_0 H)(1 - t)$, i.e. $n = 2$, and the ln $\rho - 1 / T$ becomes Arrhenius relation

$$\ln \rho(T, \mu_0 H) = \ln \rho_0(\mu_0 H) - U_0(\mu_0 H) / T,$$

(5)

where $\ln \rho_0(\mu_0 H) = \ln \rho_0 f + U_0(\mu_0 H) / T_c$ is a temperature-independent term and $U_0(\mu_0 H)$ is the apparent activation energy. Furthermore, it can be concluded that $-\ln \rho(T, \mu_0 H) / T^{-1} = U_0(\mu_0 H)$. Hence, the ln $\rho$ versus $1 / T$ should be linear in the TAFF region. The slope is $U_0(\mu_0 H)$ and its $y$-intercept represents $\ln \rho_0(\mu_0 H)$. 

As shown in figures 1(a) and (b), the experimental data can be fitted using the Arrhenius relation very well for both FeSe and Fe$_{1.03}$Te$_{0.55}$Se$_{0.45}$ (Se-45) single crystals [48, 49]. The good linear behavior indicates that the temperature dependence of $U(T, \mu_0 H)$ is approximately linear, i.e. $U(T, \mu_0 H) = U_0(\mu_0 H)(1 - \alpha T)$ [45, 46]. The log $\rho(\mu_0 H)$ lines for compounds extrapolate to the same temperature $T_{cross}$, which should be equal to $T_c$ [50]. For FeSe single crystal, the extrapolated temperatures are about 11.1 K for both $H\parallel$(101) and $H\perp$(101). This behavior has also been observed in NdFeAsO$_{0.7}$F$_{0.3}$ single crystals for $H\parallel$c, however, it is not the case for $H\parallel$ab [51]. For FeSe single crystal, the obtained $U_0$ are similar for $H\parallel$(101) and $H\perp$(101) (inset of figure 1(a)) and much smaller than in Fe(Te,Se) [49, 52]. Moreover, $\ln \rho_0(\mu_0 H) - U_0(\mu_0 H)$ is linear for both field directions (inset of figure 1(a)). Fits using $\ln \rho_0(\mu_0 H) = \ln \rho_0(\mu_0 H) + U_0(\mu_0 H)/T_c$ yielded values of $\rho_0$ and $T_c$ as 37(1) m$\Omega$ cm and 11.2(1) K for $H\parallel$(101) and 39(2) m$\Omega$ cm and 11.2(1) K for $H\perp$(101). The $T_c$ values are consistent with the values of $T_{cross}$ within the error bars. As shown in figures 1(c) and (d), the field dependence of $U_0(\mu_0 H)$ exhibits a power-law behavior for both FeSe and Se-45, i.e. $U_0(\mu_0 H) \sim (\mu_0 H)^{-\alpha}$. There are two types of power-law behavior at low and high fields. For FeSe, $\alpha \sim 0.25$ for $\mu_0 H < 3$ T and $\alpha \sim 0.7$ for $\mu_0 H > 3$ T. Se-45 exhibits similar behavior to FeSe ($\alpha \sim 0.25$ for $\mu_0 H < 2$ T and $\alpha \sim 0.55$ for $\mu_0 H > 2$ T). The weak power-law dependence of $U_0(\mu_0 H)$ at low fields implies that single-vortex pinning dominates in this region [44], followed by a quicker decrease of $U_0(\mu_0 H)$ at high fields where the vortex spacing becomes significantly smaller than penetration depth in higher fields and a crossover to a collective-pinning regime occurs. In this region, the $U_0(\mu_0 H)$ becomes strongly dependent on the field [53]. A similar crossover has been observed in Nd(O,F)FeAs single crystals [51]. Because $\alpha = 0.5$ and 1 correspond to a planar-defect pinning and a point-defect pinning, respectively [54], for FeSe, the fitted $\alpha$ values vary between 0.5 and 1, suggesting that the pinning centers may be mixed with point and planar defects. On the other hand, for Se-45, the fitted $\alpha$ values are close to 0.5, implying that the vortices are mainly pinned by the collective point defects in the high-field region.

Large fitting errors occur for Fe$_{1.14}$Te$_{0.91}$S$_{0.09}$ (S-09) single crystal when using the Arrhenius relation in the TAFF region (solid lines, especially for $H\parallel$ab (figures 2(a) and (b)). Deviation from the Arrhenius relation indicates that the assumptions of constant $\rho_0(\mu_0 H)$ and linear temperature dependence of $U(T, \mu_0 H)$ could be invalid in S-09. If $U(T, \mu_0 H) = U_0(\mu_0 H)(1 - \alpha T)$ and $\rho_0(\mu_0 H)$ = const, this will result in $-\partial \ln \rho(T, \mu_0 H)/\partial T^{-1} = U_0(\mu_0 H)$, and $U_0(\mu_0 H)$ should be a set of horizontal lines as shown in figures 2(c) and (d). The limited lengths of horizontal lines correspond to the temperature interval used for estimating $U_0(\mu_0 H)$ in the Arrhenius relation. It can be seen that $-\partial \ln \rho(T, \mu_0 H)/\partial T^{-1}$ increases sharply with decreasing temperature, which was also observed in Bi-2212 thin films [55]. The center of each $U_0(\mu_0 H)$ horizontal line approximately intersects the
\[ -\partial \ln \rho(T, \mu_0 H)/\partial T^{-1} \text{ curve, and therefore each } U_0(\mu_0 H) \text{ is only the average value of its } -\partial \ln \rho(T, \mu_0 H)/\partial T^{-1} \text{ in the fitting temperature region. Hence, the } U(T, \mu_0 H) \text{ determined using the Arrhenius relation does not reflect the true evolution of thermal activation energy with temperature in S-09, particularly for } H\parallel ab. \]

If \( \rho_{0f} = 2 \rho_c U(T, \mu_0 H)/T \) is temperature dependent due to the term \( U(T, \mu_0 H) = U_0(\mu_0 H)(1-t)^x \) and \( q \) can be different from 1, then it can be shown from equation (4) [56] that

\[ \ln \rho = \ln(2\rho_c U_0(\mu_0 H)) + q \ln(1-t) - \ln T - U_0(\mu_0 H)(1-t)^x/T \]

and thus

\[ -\partial \ln \rho/\partial T^{-1} = [U_0(\mu_0 H)(1-t)^x - T][1+qt/(1-t)], \]

where \( q, \rho_c \) and \( U_0(\mu_0 H) \) are temperature-independent free parameters, and \( T_c \) derived from the Arrhenius relation is used for fitting. Figures 2(a) and (b) reveal that all fitting curves (dashed lines) agree well with experimental data and the results are better than the Arrhenius relation, especially for \( H\parallel ab. \) Figures 2(c) and (d) clearly show the advantage of equation (7) over the Arrhenius relation. It can effectively capture the upturn trend of \(-\partial \ln \rho/\partial T^{-1}\) with decreasing temperature. As shown in figure 3(a), the \( U_0(\mu_0 H) \) values obtained using equation (6) are comparable to that in FeSe but smaller than in Fe(Te,Se) [48, 49, 52]. Similar to FeSe and Fe(Fe,Te,Se), there are also two ranges in the field dependence of \( U_0(H) \) curves with different \( \alpha \) for both field directions in S-09. For \( H\parallel ab, \alpha = 0.12(2) \) for \( \mu_0 H < 5 \ T \) and \( \alpha = 1.7(3) \) for \( \mu_0 H > 5 \ T; \) For \( H\parallel c, \alpha = 0.21(3) \) for \( \mu_0 H < 5 \ T \) and \( \alpha = 1.3(2) \) for \( \mu_0 H > 5 \ T. \) In the low-field region, the small \( \alpha \) suggests that single-vortex pinning dominates, similar to FeSe and Fe(Fe,Se). At high fields \( \alpha \) is larger, implying that the material enters a collective pinning regime and the pinning centers are point defects [54]. On the other hand, the values of \( q \) change from about 1 for \( H\parallel c \) to 2 for \( H\parallel ab \) independent on the field intensity for both directions (figure 3(b)). The value of \( q = 2 \) has also been observed in many cuprates superconductors [55–57]. The nonlinear temperature dependence of \( U_0(T, \mu_0 H) \) and non-constant prefactor \( \rho_{0f} \) are also common to other iron-based superconductors [58, 59].

It should be noted that the low volume fraction of superconductivity in Fe(Fe,S) should not significantly affect the analysis of TAFF. Because of the inhomogeneity of crystals, the conductivity can be expressed as \( \sigma = \sigma_c + \sigma_{\text{normal}}, \) where \( \sigma_c \) is the conductivity of superconducting fraction and \( \sigma_{\text{normal}} \) is the conductivity of the normal fraction.
Figure 3. Magnetic field dependences of (a) $U_c$ and (b) $\sigma$ obtained from fitting the resistivity in the TAFF region using equation (6) for Fe$_{1.14}$Te$_{0.91}$Se$_{0.09}$. The open and filled squares represent $U_c(\mu_0H)$ for $H \parallel c$ and $H \parallel ab$, respectively, while the open and filled circles show corresponding $\sigma$, respectively. The solid lines in (a) are power-law functions $U_c(\mu_0H) \sim (\mu_0H)^{-\alpha}$. Reprinted with permission from [50]. Copyright 2010 by the American Physical Society.

of the crystal. When $T < T_{c,\text{zero}}$, $\sigma = \sigma_{\text{nc}} = \infty$, i.e. $\rho = 0$ and the normal-state part of sample is short-circuited. On the other hand, the resistivity in the TAFF regime is about one to three orders of magnitude less than in the normal state [45, 46]. It means that although the conductivity $\sigma_{\text{nc}}$ in this range is finite, it is still much larger than $\sigma_{\text{normal}}$, and we can approximate $\sigma \approx \sigma_{\text{nc}}$.

In K$_{0.64}$Fe$_{1.44}$Se$_2$ and Tl$_{0.58}$Rb$_{0.42}$Fe$_{1.72}$Se$_2$ single crystals, as shown in figure 4, the good linear behavior of ln $\rho(T, \mu_0H)$ versus $1/T$ in a wide temperature range for both field directions indicates that the temperature dependence of $U(T, \mu_0H)$ is approximately linear [60], i.e. $q = 1$, and the $\rho_{\text{fj}}$ is constant, similar to FeSe and Fe(Te,Se) [48, 49]. For K$_{0.64}$Fe$_{1.44}$Se$_2$, fitting by the function $\ln \rho_0(\mu_0H) = \ln \rho_0 + U_0(\mu_0H)/T_c$ yields $\rho_0 = 5.3(1)$ and 12.4(1) $\Omega$ cm and $T_c = 31.8(3)$ and 32.3(2) K for $H \parallel ab$ and $H \parallel c$, respectively (inset of figure 4(a)). On the other hand, the log $\rho(T, \mu_0H)$ lines for different fields extrapolate to one temperature $T_{\text{cross}} \sim 32$ K for both field directions, consistent with the values of $T_c$ within the error bars. The $U_0(\mu_0H)$ values obtained for both superconductors are much larger in FeCh-11 materials; they are comparable to that in polycrystalline NdFeAsO$_{0.7}$F$_{0.3}$ [51], but are still much smaller than in polycrystalline SmFeAsO$_{0.9}$F$_{0.1}$ [58]. The power-law fitting yields $\alpha = 0.78(2)$ and 0.84(2) for $H \parallel ab$ and $H \parallel c$ in K$_{0.64}$Fe$_{1.44}$Se$_2$ and $\alpha = 0.27(2)$ for $H \parallel ab$ and 0.22(2) for $H \parallel c$ in Tl$_{0.58}$Rb$_{0.42}$Fe$_{1.72}$Se$_2$ (insets of figures 4(b)–(d)). For both materials, the field dependencies of $U_0(\mu_0H)$ are similar for both field directions, indicating that the pinning forces weakly depend on orientation [60]. But the values of $\alpha$ are rather different. For K$_{0.64}$Fe$_{1.44}$Se$_2$, the values of $\alpha$ are similar to those in FeSe, suggesting that both point and planar defects act as the pinning centers. On the other hand, the much smaller values of $\alpha$ in Tl$_{0.58}$Rb$_{0.42}$Fe$_{1.72}$Se$_2$ imply that the single-vortex pinning mechanism is dominant in fields up to 15 T.

3. Critical current density

Since the discovery of iron-based superconductors, the combination of rather high $T_c$ and high $\mu_0H_2$ has induced great interests for application. For practical applications of superconductors, however, high $J_c$ is another key parameter that needs to be investigated. YBCO has superior current-carrying properties but the stringent weak-link effect of grain boundaries (GBs) restricts the range of applications and increases the cost of fabrication [61]. In iron-based superconductors (figures 5(a) and (b)) [62], the high $\mu_0H_2$ gives some promise for applications at high fields, where low-temperature Nb$_3$Sn superconductor is at disadvantage because of low $\mu_0H_2$ [40].

Iron chalcogenide superconductors crystallize in a relatively simple crystal structure, but often with defects and relatively large range of stoichiometry. In addition, there is a sensitivity to atmosphere in AFeCh-122. However, lower anisotropy $\gamma$ of $\mu_0H_2$ when compared to iron pnictide superconductors is disadvantageous for applications such as superconducting wires for high-field magnets.

3.1. $J_c$ and flux pinning in FeCh-11 and AFeCh-122 single crystals

Figure 6 shows the $J_c$ of FeSe, FeTe$_{0.61}$Se$_{0.39}$ and FeTe$_{0.9}$Se$_{0.1}$ single crystals at various fields and temperatures [48, 63, 64]. At $T \sim 5$ K, the $J_c$ of FeSe is about $2.4 \times 10^3$ A cm$^{-2}$ for $H \perp (101)$ at zero field. This is lower than $J_c$ in FeTe$_{0.61}$Se$_{0.39}$ and FeTe$_{0.9}$Se$_{0.1}$, which is about $2 \times 10^5$ and $3 \times 10^5$ A cm$^{-2}$ for $H \parallel c$, respectively. FeTe$_{0.61}$Se$_{0.39}$ shows relative high $J_c$ and it remains above $7 \times 10^4$ A cm$^{-2}$ at $\mu_0H = 5$ T. Moreover, the $T_c$ of optimally doped Fe(FeSe) (Se $\sim 0.4 – 0.5$) is about 14 K, which is higher than in Fe(Fe,S) and FeSe. It implies that the optimally doped Fe(FeSe) might be suitable for applications. On the other hand, the anisotropy $\gamma_{J_c}$ of $J_c$ ($\gamma_{J_c} = J_c(100)/J_c(110)$ or $J_c(\parallel)/J_c(\perp)$) is about 4–5 for FeSe and FeTe$_{0.9}$Se$_{0.1}$ [48, 64].

When compared to FeCh-11 superconductors, the much higher $T_c$ and $\mu_0H_2$ of AFeSe-122 superconductors immediately raise a question whether the $J_c$ values of these materials are more promising for practical applications. As shown in figure 7(a), however, the early studies indicate that $J_c$ of K$_x$Fe$_{2-x}$Se$_2$ is rather low ($\sim (0.7-2.6) \times 10^4$ A cm$^{-2}$ at
improvement in superconducting properties also larger than in FeSe, it is still smaller than in FeTe.

Moreover, the ratio of $J_c$ of $\mathrm{Kr}_x\mathrm{Fe}_2\mathrm{Se}_2$ to that of the as-grown sample is much larger than in $\mathrm{K}_2\mathrm{Fe}_2\mathrm{Se}_2$ crystals, which is a notable feature of the quenched crystal. Therefore, it is important to explore pathways for the enhancement of $J_c$ in AFeCh-122 compounds.

It was soon found that sulfur doping can remarkably enhance the $J_c$ of $\mathrm{K}_x\mathrm{Fe}_2\mathrm{y}_z\mathrm{Se}_2$ [67]. As shown in figure 7(a), the $J_c^{\mathrm{ab}}(\mu_0H)$ at high fields is smaller. It should be noted that the $T_c$ decreases significantly when $z > 0.32$. When compared to $z = 0$, the $0.99$ crystal has $T_{\mathrm{c, onset}} = 24.6$ K, whereas $z = 1.04$ corresponds to $T_{\mathrm{c, onset}} = 18.2$ K [68]. Therefore, the sample with $z = 0.99$ exhibits the best performance among sulfur-doped samples at high fields. Moreover, the ratio of $J_c^{\mathrm{ab}}(\mu_0H)/J_c^{\mathrm{ab}}(\mu_0H)$ is approximately 1 and is smaller in Fe-Ch-11 superconductors. Although the $J_c$ of $z = 0$ sample is much larger than in $\mathrm{K}_x\mathrm{Fe}_2\mathrm{Se}_2$ and also larger than in $\mathrm{FeSe}$, it is still smaller than in $\mathrm{FeTe}_{0.61}\mathrm{Se}_{0.39}$ and $\mathrm{FeTe}_{0.6}\mathrm{S}_{0.1}$.

Metallic and superconducting state was induced by post-annealing and quenching treatment in as-grown and sulfur-doped $\mathrm{K}_x\mathrm{Fe}_2\mathrm{Se}_2$ crystals, which is a notable improvement in superconducting properties [69]. Therefore, some effects of this process on the $J_c$ are also expected [70]. Post-annealing and quenching process can further increase $J_c^{\mathrm{ab}}(0)$ to $7.4 \times 10^3$ A cm$^{-2}$ at 1.8 K which is about 50 times larger than that of the as-grown sample (figure 4(a)). This cannot be simply ascribed to the improvement of the superconducting volume fraction, because the volume fraction of the quenched crystal is only about four times larger than that of the as-grown crystal. It could also be related to the enhanced flux pinning force due to the post-annealing and quenching treatment. The $J_c$ in the quenched crystal is slightly higher than that in $\mathrm{K}_x\mathrm{Fe}_2\mathrm{y}_z\mathrm{Se}_2$ crystals grown using the one-step technique [71] and are the highest known $J_c$ values among AFeCh-122 type materials until now. The quenched sample also exhibits a good performance at high fields. The $J_c^{\mathrm{ab}}(\mu_0H = 4.8$ T) for the quenched sample is still larger than $10^3$ A cm$^{-2}$ at 1.8 K, whereas for the as-grown sample, it has already decreased about one order of magnitude.

As shown in figure 7(b), detailed studies on the temperature and field dependences of the vortex pinning force $F_p = \mu_0HJ_c$ show that it follows the Dew-Hughes [72] scaling law: $f_p \propto h^{(1−h)q}$, where $f_p = F_p/F_{\mathrm{p,max}}$ is the normalized vortex pinning force, $F_{\mathrm{p,max}}$ corresponds to the maximum pinning force and $h = H/H_{\mathrm{m}}$ is the reduced field. The results indicate that there is a dominant pinning mechanism. The obtained $p = 0.36(1)$ and $1.83(2)$, respectively and the value of $h_{\mathrm{m,max}} = p/(p+q) \approx 0.32$ is consistent with the peak positions ($h_{\mathrm{m}} \approx 0.33$) of the experimental curves at different temperatures. Those values are close to the expected values for core normal point-like

![Figure 4](image-url)
pinning (\(p = 1, q = 2\) and \(h_{\text{fit}}^{\text{max}} = 0.33\)) [69]. These point-like pinning centers might come from the random distribution of iron vacancies after quenching, similar to FeAs-122 type materials [73, 74]. On the other hand, the \(F_p^{\text{max}}\) can be fitted using \(F_p^{\text{max}} \propto (\mu_0 H_{\text{fit}})^{0}\) with \(\alpha = 1.67(1)\) (inset of figure 4(b)), close to the theoretical value (\(\alpha = 2\)) for the core normal point-like pinning [72]. Moreover, as shown in figure 7(c), the temperature dependence of \(\mu_0 H_{\text{fit}}\) can be fitted with equation \(\mu_0 H_{\text{fit}}(T) = \mu_0 H_{\text{fit}}(0)(1 - T)^\beta\), and we obtained \(\beta = 1.21(1)\), close to the characteristic value of 3D giant flux creep (\(\beta = 1.5\)) [53]. For type-II superconductors, vortices interact with pinning centers either via the spatial variations in the \(T_c\) (‘\(\delta T_c\) pinning’) or by scattering of charge carriers with reduced mean free path \(l\) near defects (‘\(\delta l\) pinning’) [44]. These two pinning types result in the different temperature dependences of \(J_c(t)\) in the single vortex pinning regime i.e. low-field and zero-field regions. For \(\delta T_c\) pinning, \(J_{c,H=0}^{\text{fit}}(t) = J_{c,H=0}(0)(1 - t^2)^{5/6}(1 + t^2)^{5/6}\) for \(\delta l\) pinning, \(J_{c,H=0}^{\text{fit}}(t) = J_{c,H=0}(0)(1 - t^2)^{5/2}(1 + t^2)^{-1/2}\) [77]. As shown in figure 3(c), the \(J_{c,H=0}(t)\) is between the two curves corresponding to \(\delta T_c\) and \(\delta l\) pinnings, respectively, but much closer and similar in shape to the \(\delta T_c\)-pinning curve. Using \(J_{c,H=0}(t) = x J_{c,H=0}^{\text{fit}}(t) + (1 - x) J_{c,H=0}^{\text{fit}}(t)\), the experimental data can be fitted very well with \(x = 0.74(2)\), suggesting that both \(\delta T_c\) and \(\delta l\) pinning play roles in the quenched K\(_x\)Fe\(_{2-y}\)Se\(_2\) single crystals, but the former mechanism is dominant. The dominant effect of \(\delta T_c\) pinning also implies that the main pinning centers lead to the distribution of \(T_c\) in their vicinity or might even be non-superconducting, like Y\(_2\)O\(_3\) and Y–Cu–O precipitates in YBa\(_2\)Cu\(_3\)O\(_{7-x}\) thin films [78]. Although the
Figure 7. (a) Field dependences of $J_c^b(μ_0 H)$ of sulfur-doped K$_x$Fe$_{2−y}$Se$_2$−S and quenched K$_x$Fe$_{2−y}$Se$_2$ single crystals at 1.8 K. (b) Reduced field dependence of $f_p(h)$ at various temperatures for quenched K$_x$Fe$_{2−y}$Se$_2$ single crystal. Solid line is fitting curve using $f_p = A h^{5/6} (1−h)^{7/6}$. Inset: $F_p^{max}$ as a function of $H_{irr}$. The fitting result using $F_{p}^{max} = A (μ_0 H_{irr})^{γ}$ is shown as solid lines. (c) Reduced temperature dependence of $μ_0 H_{irr}(t)$ with the fitting result using the (1 − $t^2$)$^{5/6}$ law (solid line) for quenched K$_x$Fe$_{2−y}$Se$_2$ single crystal. (d) Reduced temperature dependence of the $J_c(t)$ at zero field for quenched K$_x$Fe$_{2−y}$Se$_2$ single crystal. The solid line shows the fitting result using $J_c(0)(1−t^2)^{5/6}$. The measured and estimated $μ_0 H_{irr}$ are shown as filled and open circles in inset of (b) and (c). Reprinted with permission from [70]. Copyright 2011 by the American Physical Society.

$J_c^b$ of quenched K$_x$Fe$_{2−y}$Se$_2$ single crystals is enhanced significantly when compared to the as-grown samples, it is still smaller than in FeTe$_{0.64}$Se$_{0.36}$ and other iron pnictide superconductors [73, 74]. There might be more room to improve the current-carrying capacity for AFeCh-122 superconductors in the future using methods such as A site ionic disorder and nanometer-scale second phases.

It should be noted that if the phase separation scale is microns or even larger, the insulating region could have some effect on the calculation of the absolute values of $J_c$. This is because the volume of insulating phase has been used to calculate the $J_c$ from $M−H$ curve, i.e., the real $J_c$ values might be even larger than the calculated ones. However, the phase separation should have minor effects on the field and temperature dependences of $J_c$, i.e. the pinning mechanism should not be affected by this type of phase separation. If the phase separation occurs in the nanometer range, it has been observed in K$_x$Fe$_{2−y}$Se$_2$ by transmission electron microscopy [75], the effects on $J_c$ are similar to what has been discussed above regarding the pinning mechanism. The insulating second phase can be considered as the pinning center, similar to nanometer-scale BaZrO$_3$ inclusions in YBCO coatings on metals [76].

3.2. GBs properties of iron-based superconductors

For practical applications, especially for fabrication of superconducting wires and tapes, superconductors are usually made in the polycrystalline bulk or thin-film form. Therefore, besides enhancement of $J_c$ by various artificial pinning centers in the grains, i.e. enhancement of intragrain properties, the GBs properties are also of great interest for the applications of iron-based superconductors.

There are two studies so far on the Ba(Fe$_{1.2}$Co$_{0.8}$)$_2$As$_2$ epitaxial thin films deposited on bicrystal substrates (figure 8) [79, 80]. Both show that the $J_c$ across bicrystal grain boundary (BGB) has an exponential dependence on GB misorientation angle $θ$, indicating a weak-link effect for high-angle BGBs. However, the critical GB misorientation angles $θ_c$ are different: about 6° and about 10° [79, 80]. According to the study of Katase et al., the slopes of the exponential decays are much smaller than those for YBCO BGBs, and the critical angle is approximately 9–10°, which is substantially larger than that of YBCO (~3–5°, inset of figure 8(a)) [80, 81]. Larger critical angle suggests smaller constraints for the in-plane orientation for substrate or buffer layers to obtain high-$J_c$ iron-based superconducting films on flexible metal substrates. This observation will certainly be advantageous for tape applications. Similar study is lacking in
immediately carried out for fabrication of iron-based superconducting wires were after the discovery of iron-based superconductors, the trials for fabrication of iron-based superconducting wires were immediately carried out \[82\text{–}84\]. There are two methods to prepare iron-based superconducting wires and tapes, power-in-tube (PIT) and coated conductor techniques.

PIT technique has been used widely in Bi-based cuprate oxide wires (first-generation high-temperature superconductor (HTS) wires) and MgB\textsubscript{2} \[85, 86\]. Ozaki et al.\[87\] fabricated Fe(Se,Te) wires by an \textit{ex situ} PIT method with the transport \(J_c(0)\) of about 64 A cm\textsuperscript{−2} at 4.2 K. Recently, chemical-transformation PIT method was used to fabricate FeSe wires with a transport \(J_c(0)\) of 588 A cm\textsuperscript{−2} at 4.2 K for a three-core wire (figure 9(a)) \[88\]. Although the \(J_c\) is enhanced considerably, it is much smaller than that of iron arsenic superconducting wires prepared using PIT method. For example in (Ba,K)Fe\textsubscript{2}As\textsubscript{2} the \(J_c(0)\) reaches \(1 \times 10^7\) A cm\textsuperscript{−2} at 4.2 K \[89\]. But it should be noted that the \(J_c\) for both iron chalcogenide and iron arsenic superconducting wires fabricated using PIT method are much smaller than those of single crystals \[48, 63, 74\], implying that the texturing of grains in wires is important due to the GB weak-link effect.

Coated conductor technique has been successfully developed for the YBCO coated conductors (second-generation HTS wires) to overcome the weak-link effect \[61\]. The FeSe\textsubscript{0.5}Te\textsubscript{0.5} thin films deposited on Hastelloy substrates, on which an MgO buffer layer has been formed by iron beam assisted deposition (IBAD), exhibit a nearly isotropic \(J_c(0)\) exceeding \(2 \times 10^5\) A cm\textsuperscript{−2} at 4.2 K and still higher than \(1 \times 10^4\) A cm\textsuperscript{−2} at a magnetic field as high as 25 T (figure 9(b)) \[90\]. This gives the superior property in high fields (\(\geq 20\) T) when compared to Nb\textsubscript{3}Sn or Ni–Ti wires. The fitting of field dependency of the \(F_p\) using Dew-Hughes scaling law yields \(q \sim 2\) and \(p \sim 1\) (figure 9(c)), similar to K\textsubscript{Fe\textsubscript{2}−\textit{y}(Se,S)\textsubscript{2}} and quenched K\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} \[67, 70\]. This suggests that the point-defect core pinning is dominant due to the inhomogeneous distribution of Se and Te \[90\]. In the core-pinning regime, \(F_p\) is a product of the individual \(F_{p,\text{ind}}\) and the pinning center density \(n\). This implies that the \(J_c\) of FeSe\textsubscript{0.5}Te\textsubscript{0.5} thin films can still be enhanced by simply adding more defects to act as pinning centers \[90\]. Moreover, the weak-link effect of FeSe\textsubscript{0.5}Te\textsubscript{0.5} may not be as severe as that of YBCO. Although the IBAD substrates have many low-angle GBs in the textured MgO template, the \(J_c(0)\) of FeSe\textsubscript{0.5}Te\textsubscript{0.5} thin films on IBAD-MgO with in-plane misorientation angle \(\Delta \phi = 4.5^\circ\) is just a little lower than that of thin films deposited on LaAlO\textsubscript{3} single-crystal substrate \[90\]. These results should be confirmed with further studies of the thin films grown on controlled bicrystal substrates. On the other hand, depositing FeSe\textsubscript{0.5}Te\textsubscript{0.5} thin films directly on textured metal tapes may be possible because FeSe\textsubscript{0.5}Te\textsubscript{0.5} thin films are prepared in vacuum unlike YBCO-coated conductors. This considerably simplifies the synthesis procedure and reduces production costs \[62\]. A similar study on the Ba(Fe,Co)\textsubscript{2}As\textsubscript{2} thin films deposited on IBAD-MgO-buffered Hastelloy substrates shows that the \(J_c(0)\) is \((1.2\text{–}3.6) \times 10^6\) A cm\textsuperscript{−2} at 2 K with \(\Delta \phi \sim 3^\circ\), regardless of the larger \(\Delta \phi(5.5\text{–}7.3^\circ)\) of the MgO buffer layers \[91\]. It is much larger than that of Ba(Fe,Co)\textsubscript{2}As\textsubscript{2} wire prepared by PIT method and comparable to that on MgO single crystals and remains at \(1 \times 10^6\) A cm\textsuperscript{−2} at \(T \leq 10\) K \[89, 91\]. This observation is consistent with the fact that the \(\Delta \phi\) of Ba(Fe,Co)\textsubscript{2}As\textsubscript{2} is much smaller than the \(\theta_i = 9^\circ\) \[91\]. These results demonstrate that the coated conductors

**Figure 8.** (a) Dependence of the intergrain \(J_{c,\text{gb}}(12\text{ K}, 0.5\text{ T}, \theta)\) on the misorientation angle \(\theta\) for Ba(Fe,Co)\textsubscript{2}As\textsubscript{2} BGB junction. Inset shows the \(J_{c,\text{gb}}(\theta)\) for YBCO. (b) \(J_{c,\text{gb}}(\theta)\) for Ba(Fe,Co)\textsubscript{2}As\textsubscript{2} BGB junctions grown on [001]-tilt bicrystal substrates of MgO (open symbols) and (La,Sr)(Al,Ta)O\textsubscript{3} (filled symbols) at 4 K (red symbols) and 12 K (blue symbols). The red and blue solid lines are fitted to the empirical equation of \(J_{c,\text{gb}} = J_c \exp(−\theta_{\text{gb}}/\theta_\text{c})\). The average data of the YBCO BGB junctions taken at 4 and 77 K are indicated by the green and orange dashed lines, respectively. The inset shows the ratio of the intragrain \(J_{c,\text{gb}}\) and \(J_{c,\text{gb}}\) to \(\theta_{\text{gb}}\) at 4 K on MgO (open circle) and (La,Sr)(Al,Ta)O\textsubscript{3} (filled triangle) bicrystals, respectively. The dashed green line shows the result of the YBCO BGB junctions. (a) Reprinted with permission from \[79\]. Copyright 2009 by the American Institute of Physics. (b) Reprinted with permission from \[80\]. Copyright 2011 by the Macmillan Publishers Ltd: Nature Comm.

iron selenide superconductors, and therefore related studies on FeCh-11 or AFeCh-122 films will be of interest to understand the GB properties.

### 3.3. Iron chalcogenide superconducting wires and tapes

After the discovery of iron-based superconductors, the trials for fabrication of iron-based superconducting wires were immediately carried out \[82–84\]. There are two methods to prepare iron-based superconducting wires and tapes, power-in-tube (PIT) and coated conductor techniques.
Figure 9. (a) Field dependence of $J_c(B)$ for single-core and three-core FeSe wires. (b) $J_c(B)$ and (c) $F_p(B)$ of FeSe$_{0.5}$Te$_{0.5}$ thin films at 4.2 K compared with the results of other superconducting wires or tapes. Solid lines in (c) are the fitting results using the Dew-Huges’s scaling law. (a) Reprinted with permission from [88]. Copyright 2011 by the IOP Publishing. (b) Reprinted with permission from [90]. Copyright 2011 by the American Institute of Physics.

Figure 10. (a) Schematics of depairing mechanism of a singlet Cooper pair via the external magnetic field. (b) Schematic field dependences of the Gibbs free energies of the normal state and superconducting state in a type-II superconductor. The free-energy curve of the normal state without Zeeman energy is the upper horizontal line, crossing the free-energy curve of a type-II superconductor at $B^{*}_{c2}$. The free-energy curve of the normal state including Zeeman energy is the red line, crossing the free-energy curve of a type-II superconductor at $B^{p}_{c2}$ and the zero-field free-energy curve of the superconducting state (lower horizontal line) at the Pauli limiting field $B^{p}$. Reprinted with permission from [92]. Copyright 2009 by the IOP Publishing.

technique is a promising method to fabricate iron-based superconducting tapes for high field applications.

4. Upper critical fields

The upper critical field $\mu_0H_{c2}$ is one of the most important superconducting parameters which provides valuable information on fundamental superconducting properties, such as coherence length, anisotropy, details of underlying electronic structures and dimensionality of superconductivity as well as insights into the pair-breaking mechanism. Iron-based superconductors usually have very high $\mu_0H_{c2}$ and exhibit rich variety of temperature dependence of $\mu_0H_{c2}(T)$.

4.1. Pair breaking mechanisms and multiband effects on $\mu_0H_{c2}$

The s wave Cooper pair is formed by two electrons that attract together with opposite spins and momenta. External magnetic fields contributes to depairing via two primary mechanisms (figure 10(a)) [92]. One is the orbital pair breaking mechanism. The Lorentz force acts on paired electrons with opposite momenta and the superconductivity is destroyed when the kinetic energy exceeds the condensation energy of the Cooper pairs. Another mechanism...
is the Pauli paramagnetic pair breaking. When the Pauli spin susceptibility energy (Zeeman energy) exceeds the condensation energy as shown in figure 10(b), the singlet pair with opposite spins is broken into unbound triplet along the field direction (Zeeman effect, also called spin-paramagnetic effect).

Through the Maki parameters $\alpha$ (see below) and $\lambda_{so}$ [93], the effects of Pauli spin paramagnetism and spin-orbital scattering have been included in the Werthamer–Helfand–Hohenberg (WHH) theory for a single-band $s$ wave weak-coupled type-II superconductor in the dirty limit [94]. The $\mu_0 H_{c2}(T)$ is given by

$$\ln \frac{1}{t} = \left( \frac{1}{2} + \frac{\lambda_{so}}{4\gamma} \right) \psi \left( \frac{1}{2} + \frac{h + \lambda_{so}/2 + i\gamma}{2t} \right) + \left( \frac{1}{2} - \frac{i\lambda_{so}}{4\gamma} \right) \psi \left( \frac{1}{2} + \frac{h + \lambda_{so}/2 - i\gamma}{2t} \right) - \psi \left( \frac{1}{2} \right).$$

(8)

where $\psi(x)$ is digamma function, $\gamma \equiv [(ah)^2 - (\lambda_{so}/2)^2]^{1/2}$ and $h = 4\mu_0 H_{c2}(T) / \pi^2 T_c (-d\mu_0 H_{c2}(T)/dT)_{T=T_c}$. (9)

If the orbital effect is dominant ($\alpha = 0$) and the spin-orbital scattering is negligible ($\lambda_{so} = 0$), the equation can be simplified as

$$\ln \frac{1}{t} = \psi \left( \frac{1}{2} + \frac{h}{2t} \right) - \psi \left( \frac{1}{2} \right),$$

(10)

which describes the temperature dependence of orbital limited upper critical field $\mu_0 H_{c2}^*(T)$. At zero temperature it becomes

$$\mu_0 H_{c2}^*(0) = -0.693 T_c (d\mu_0 H_{c2}(T)/dT)_{T=T_c}.$$  

(11)

On the other hand, if we only consider the spin-paramagnetic effect alone, the zero-temperature Pauli limiting field $\mu_0 H_p(0)$ (Chandrasekhar–Clogston limit field for a weakly coupled superconductor) is [95, 96]

$$\mu_0 H_p(0)|T = \Delta / \sqrt{2}\mu_B = 1.86 T_c,$$

(12)

where $\Delta$ is the $s$ wave superconducting gap. Including strong-coupling corrections in the BCS theory due to electron–phonon and electron–electron interactions gives [92, 97]

$$\mu_0 H_p(0)|T = 1.86(1 + \lambda_{ep})^{\alpha} n_A n_B (1 - I).$$

(13)

Here $n_A$ describes the strong coupling intraband correction for the gap, $I$ is the Stoner factor $I = N(E_F) J$, $N(E_F)$ is the electronic density of states (DOS) per spin at the Fermi energy $E_F$, $J$ is an effective exchange integral, $n_B$ is introduced to describe phenomenologically the effect of the gap anisotropy, $\lambda_{ep}$ is electron–phonon coupling constant and $\varepsilon = 0.5$ or 1 [92, 97, 98].

When compared to the orbital pair breaking effect, the relative contribution of the Pauli paramagnetic pair breaking effect is quantified by the Maki parameter $\alpha = \sqrt{2} H_{c2}^*(0)/H_p(0)$. When $\alpha > 1$, the spin-paramagnetic effect becomes essential [93] and the actual upper critical field $\mu_0 H_{c2}(0)$ is given by

$$\mu_0 H_{c2}(0) = \mu_0 H_{c2}^*(0) / \sqrt{1 + \alpha^2}.$$  

(14)

In the single-band clean limit, the Maki parameter $\alpha$ is given by [40]

$$\alpha = \frac{\pi^2 \Delta m}{4 E_F m_0}, H || c,$$

(15)

$$\alpha = \frac{\pi^2 \Delta m v_{ab}}{4 E_F m_0 v_c}, H || ab,$$

(16)

where $v_{ab}$ and $v_c$ are the Fermi velocities in the $ab$ plane and along the $c$-axis, respectively, $m$ is the electron effective mass and $m_0$ is free electron mass. For conventional single-band BCS superconductors, because of $m \sim m_0$, $v_{ab} \sim v_c$, and low $T_c$, the $\alpha$ is usually small, i.e. the orbital pair breaking mechanism is dominant. On the other hand, for some exotic superconductors, such as heavy fermion superconductors with $m \gg m_0$ or organic superconductors with large ratio of $v_{ab}/v_c$, the condition of $\alpha > 1$ can be easily satisfied and the spin-paramagnetic effect is dominant. When $\alpha$ is large enough and superconductors are in the clean limit, the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state may appear, resulting in a non-zero momentum of the Cooper pairs and the spatial oscillations of the superconducting order parameter [99, 100].

On the other hand, for the superconductors with several disconnected Fermi surfaces, the multiband effects on the $\mu_0 H_{c2}$ should be considered. The most famous example is MgB$_2$ where the $\mu_0 H_{c2}$ can be described successfully using the two-band BCS model in the dirty limit [101, 102].

In the dirty limit, taking into account both orbital and spin-paramagnetic effect with interband and intraband scattering contributions, the $\mu_0 H_{c2}(T)$ is given by

$$\lambda_{0} + \lambda_{i}(\ln t + U_{+}) + (\lambda_{0} - \lambda_{i})(\ln t + U_{-}) + 2w(\ln t + U_{+})(\ln t + U_{-}) = 0,$$

(17)

where $t = T / T_{20}$, and

$$\lambda_{0} = (\lambda_{2}^{\pm} \pm 4\lambda_{12}^{\pm} \lambda_{21})^{1/2},$$

(18)

$$\lambda_{i} = [(\omega_{+} - \gamma_{-}) \lambda_{+} - 2\lambda_{12}^{\pm} \gamma_{21} - 2\lambda_{21}^{\pm} \gamma_{12}] / \Omega_{0},$$

(19)

$$\lambda_{\pm} = \lambda_{11} \pm \lambda_{22},$$

(20)

$$\omega_{\pm} = (D_{1} \pm D_{2}) \pi \mu_0 H_{c2}/\Phi_0,$$

(21)

$$\gamma_{\pm} = \gamma_{12} \pm \gamma_{21},$$

(22)

$$\Omega_{0} = [\omega_{+}^{2} + 4\gamma_{21}^{2}]^{1/2},$$

(23)

$$w = \lambda_{12} \lambda_{22} - \lambda_{12} \lambda_{21},$$

(24)
4.2. Features of $\mu_0 H_{c2}(T)$ in iron arsenic superconductors

All parameters of equations (15) and (16) that might lead to a large $\alpha$ exist in iron-based superconductors \[40\], therefore the spin-paramagnetic effect needs to be considered. Furthermore, there are several disconnected electron and hole sheets at the FS that originate from the hybridized d-orbitals of iron \[29\]. This suggests that the multiband effect on the $\mu_0 H_{c2}(T)$ should also be taken into account. For iron arsenic superconductors, due to the different contributions of multiband and spin-paramagnetic effects, there are various temperature dependences of $\mu_0 H_{c2}(T)$ for different systems (see the review paper about this topic \[103\] and references therein). Figure 11 shows several typical $\mu_0 H_{c2}(T)$ dependences in iron arsenic superconductors. FePt-1111 system (LnFeAs(O,F), figure 11(a)) shows a pronounced upturn curvature in $\mu_0 H_{c2,c}(T)$ at low temperatures. In contrast, $\mu_0 H_{c2,ab}(T)$ exhibits a downturn curvature with decreasing temperature \[51, 104\]. Both can be explained within a two-band theory with a high diffusivity ratio of electron band to hole band, but the spin-paramagnetic effect also needs to be considered, especially for $H \parallel ab$ \[51, 104, 105\]. For the FeAs-122 system (A(Fe,Co)$_2$As$_2$, figure 11(b)), the upturn curvature of $\mu_0 H_{c2,ab}(T)$ present in FeAs-1111 system does not appear, but it still shows a positive curvature.
at temperatures far below $T_c$ without saturation. On the other hand $\mu_0 H_{c2,ab}(T)$ tends to saturate with decreasing temperature [106, 107]. This can also be interpreted using a two-band theory with a larger diffusivity ratio of two bands when compared to FePn-1111 system [106, 107]. Similar to FePn-1111 system, the spin-paramagnetic effect may also have some effect on the $\mu_0 H_{c2,ab}(T)$ [107]. For KFe$_2$As$_2$ and LiFeAs (figures 11(c) and (d)), both $\mu_0 H_{c2,ab}(T)$ and $\mu_0 H_{c2,c}(T)$ show saturation trends at low temperatures with different negative curvatures. The former can be ascribed to the spin-paramagnetic effect and the latter is mainly determined by the orbital-limited field in the one-band scenario [108, 109].

4.3. Features of $\mu_0 H_{c2}(T)$ in iron chalcogenide superconductors

Both multiband and spin-paramagnetic effects contribute to $\mu_0 H_{c2}(T)$ in iron chalcogenide superconductors. However, the multiband effect is much weaker when compared to iron arsenides, and the spin-paramagnetic effect is usually the dominant factor.

In Fe(Te,Se) (as shown on examples of Fe$_{1.02}$Te$_{0.61}$Se$_{0.39}$ (Se-39) and Fe$_{1.05}$Te$_{0.89}$Se$_{0.11}$ (Se-11) in figures 12(a) and (b)) both $\mu_0 H_{c2}(T)$ for $H||ab$ and $H||c$ can be explained well using the WHH model with spin-paramagnetic effect when neglecting spin-orbital scattering. It indicates that the spin-paramagnetic effect is the dominant pair-breaking mechanism for both $H||ab$ and $H||c$ [110, 111, 114]. For the Fe(Te,Se) in the clean limit (grown by Bridgman–Stockbarger technique) the $\mu_0 H_{c2}(T)$ is Pauli limited. This may suggest the emergence of the FFLO state at low temperatures [114]. The dominance of spin-paramagnetic effect in Fe(Te,Se) may be due to the disorder induced by Te(Se) substitution/vacancies and excess Fe in Fe(2) site [92, 115]. For Se-39, more Se doping introduces more disorder than in Se-11. This effect could contribute to the larger $\alpha_{H||ab}$ of Se-39 when compared to Se-11. However, it cannot explain the inverse trend of $\alpha_{H||c}$.

Therefore, another effect must compete with disorder. It may be the effect of excess Fe in Fe(2) position, which is the unique feature of 11-system, different from other Fe pnictide superconductors. The Fe(2) has larger local magnetic moment than Fe(1) in Fe-(Te,Se) layers. The Fe(2) moment is present even if the SDW antiferromagnetic ordering of the Fe plane is suppressed by doping or pressure, contributing to $N(E_F)$ [25]. According to equation (13), $\mu_0 H_{c0}(0)$ can be decreased if the Stoner factor increases via enhancement of $J_N$ or $N(E_F)$. Excess Fe in Fe(2) site with local magnetic moment could interact with itinerant electron in Fe layer, resulting in exchange-enhanced Pauli paramagnetism or Ruderman–Kittel– Kasuya–Yosida (RKKY) interaction, thus enhancing $J$. Hence, higher content of excess Fe in Se-11, could lead to larger $\alpha_{H||c}$ than in Se-39. Another possibility may be that the $N(E_F)$ is decreased with increasing the content of Se [116]. This trend

![Figure 12. Temperature dependence of $\mu_0 H_{c2}(T)$ for Fe$_{1.02}$Te$_{0.61}$Se$_{0.39}$, Fe$_{1.05}$Te$_{0.89}$Se$_{0.11}$, Fe$_{1.05}$Te$_{0.89}$Se$_{0.11}$, and FeSe single crystals. Insets: the anisotropy $\gamma$ of $\mu_0 H_{c2}(T)$.](http://example.com/figure12)
Temperature dependence of \(\mu_0H_{c2}(T)\) near \(T_{c0}\) for (a) \(K_{0.65}Fe_{1.44}Se_2\), (b) \(Rb_{0.42}Fe_{1.44}Se_2\), (c) \(Cs_{0.41}Fe_{1.44}Se_2\) and (d) \(Tl_{0.5}Rb_{0.42}Fe_{1.44}Se_2\) single crystals. (b) Reprinted with permission from [123] and (c) Reprinted with permission from [124]. Copyright 2011 by the American Physical Society. (d) Reprinted with permission from [123]. Copyright 2011 by the European Physical Society.

Figure 13. Temperature dependence of \(\mu_0H_{c2}(T)\) near \(T_{c0}\) for (a) \(K_{0.65}Fe_{1.44}Se_2\), (b) \(Rb_{0.42}Fe_{1.44}Se_2\), (c) \(Cs_{0.41}Fe_{1.44}Se_2\) and (d) \(Tl_{0.5}Rb_{0.42}Fe_{1.44}Se_2\) single crystals. (b) Reprinted with permission from [123] and (c) Reprinted with permission from [124]. Copyright 2011 by the American Physical Society. (d) Reprinted with permission from [123]. Copyright 2011 by the European Physical Society.

will also enhance the Pauli-limited field, i.e. suppress the spin-paramagnetic effect.

As shown in figure 12(c), spin-paramagnetic effect is also dominant in \(\mu_0H_{c2}(T)\) of S-09 with larger \(\alpha\) and obvious spin-orbital scattering [117], when compared to Se-39 and Se-11. The spin-paramagnetic effect should have the same origin as in Se-39 and Se-11 due to disorder. Moreover, since the \(N(E_F)\) of FeS is larger than that of FeSe, [116], it is likely that the \(N(E_F)\) of S-09 is larger than that of Fe(Te,Se) with the same doping content. This will lead to the smaller \(\mu_0H_{c0}(0)\), i.e. larger \(\alpha\). On the other hand, non-zero \(\lambda_{so}\) can also be explained via increasing Kondo-like scattering from excess Fe in Fe(2) site, consistent with the definition of \(\lambda_{so}\), which is proportional to the spin-flip scattering rate [93, 94]. It is also consistent with the Kondo behavior of S-09 in the normal state, related to the excess Fe in Fe(2) that act as the Kondo-like impurities [117]. The presence of Kondo-type interactions in binary iron chalcogenides, first inferred from the normal-state scattering and \(\mu_0H_{c2}(T)\) behavior, has later been confirmed by the neutron scattering measurements [118].

Furthermore, the evaluated mean free path of S-09, \(l = 1.35\) nm using the Drude model \(l = \frac{\hbar(3\pi^2k^2/3)}{e^2}\rho_0n_0^{2/3}\), suggests that S-09 is a dirty-limit superconductor since \(l/\xi(0) = 0.396\) [117]. Therefore, the FFLO state at high fields is unlikely in S-09 because the short mean free path will remove any momentum anisotropy [99, 100].

The \(\mu_0H_{c2,2,0}(T)\) of FeSe single crystal at low temperatures is larger than the value evaluated from the WHH theory with \(\alpha = 0\) and \(\lambda_{so} = 0\) (figure 12(d)) [119], which is distinctively different from Fe(Te,Se) and Fe(Te,S) where the WHH curve is far above the experimental data. The enhancement of the \(\mu_0H_{c2}(T)\) at low temperatures and high fields implies that the multiband effect is not negligible. By using the coupling constants, determined from muon spin resonance (\(\mu SR\)) experiment with very small interband coupling [120], the \(\mu_0H_{c2,2,0}(T)\) data from both \(rf\) and resistivity measurements can be very well explained using a two-band model with \(\eta = 0.40\). It is similar to the value of FeAs-122 but much larger than that of other two-band iron-based superconductors, such as FeAs-1111 [51, 104]. Large \(\eta\) leads to the absence of the upturn of \(\mu_0H_{c2}(T)\) at low temperatures, which is observed in FeAs-1111 superconductors [51, 104], but not in FeAs-122 compounds [106]. We have also performed simulations for different values of coupling constants: (i) dominant intraband coupling, \(w > 0\) and (ii) dominant interband coupling, \(w < 0\). The different sets of fitting parameters results in almost identical result, fitting the experimental data well (figure 12(d)). The derived \(\eta\) is in the range of 0.32–0.44, suggesting that the fitting results are insensitive to the choice of coupling constants. Thus, either interband and intraband coupling strength are comparable or their difference is below the resolution of our experiment. On the other hand, assuming \(\mu_0H_{c2,2,0}(T = 0.35\) K) \(\approx \mu_0H_{c2}(0)\), the \(\mu_0H_{c2}(0)\) are 17.4(2) and 19.7(4) T for \(H \parallel (101)\) and \(H \perp (101)\), respectively. Given the electron–phonon coupling
parameter $\lambda \sim 0.5$ (typical value for weak-coupling BCS superconductors) [121], the Pauli limiting field $\mu_0 H_0(0) = 1.86 T_\perp (1 + \lambda \sim 0.5) / 2$ is 19.8 T [97]. This is nearly the same as the $\mu_0 H_0(T) (T = 0.35 \text{ K})$ and larger than value for $H_\perp (101)$. It suggests that the spin-paramagnetic effect might also have some influence on the $\mu_0 H_0(T)$, but should not be the dominant effect. The situation is rather different in Fe(Se,Te) and Fe(Se,S) where the spin-paramagnetic effect governs $\mu_0 H_0(T)$ [110, 117]. The existence of two bands is also confirmed from the Hall measurement [119].

The anisotropy of $\mu_0 H_0(T)$, $\gamma(T) = H_{ab}(T)/H_{c2}(T)$ (insets of figures 12(a)–(c)) decreases with decreasing temperature, reaching $\sim 1$ for all Fe(Se,Te) and Fe(Se,S) compounds. Similar results have been reported in the literature [66, 122]. These results show that Fe(Se,Te) and Fe(Se,S) are high-field isotropic superconductors. When $T$ is close to $T_c$, the $\gamma$ of Se-11 is smaller than that of Se-39 but larger than in Fe(Se,S). Although the behavior of $\gamma(T)$ is similar in Fe(Se,Te)/Fe(Se,S) and FeAs-based superconductors, the value is smaller in the former compounds [103]. For FeSe, the $\gamma(T) = (H_{ab}(H_\perp (101)) / H_{c2}(H_\perp (101))$ is nearly constant and close to 1, but it is difficult to compare this with other FeCh-11 superconductors due to the differences of the orientation.

In AFeCh-122 superconductors, the slopes of $\mu_0 H_0(T)$ near $T_{c0}$, $d\mu_0 H_0(T) / dT |_{T = T_c} (\sim 6 - 10 \text{ T K}^{-1})$ are similar to those in FeCh-11 materials for $H_\parallel ab$ but are much smaller ($\sim 1 - 3 \text{ T K}^{-1}$) than in the latter for $H_\parallel c$ (figure 13) [60, 110, 117, 123–125]. The larger $T_c$ compared to FeCh-11 superconductors leads to the significantly larger $H_{c2}(0)$ evaluated from equation (11) for $H_\parallel ab$. The $\mu_0 H_0(T)$ values are usually $\sim 125 - 275 \text{ T}$ and $\sim 30 - 60 \text{ T}$ for $H_\parallel ab$ and $H_\parallel c$, respectively [60, 123, 125].

Recent studies on the $\mu_0 H_0(T)$ of $K_{0.8}Fe_{1.76}Se_2$ and $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ single crystals up to 60 T show that $\mu_0 H_0(T)$ for $H_\parallel c$ presents an almost linear temperature dependence and slight upturn at low temperatures, whereas the curve of $\mu_0 H_0(T)$ for $H_\parallel ab$ has a convex curvature with a much larger value and gradually tends to saturate at low temperatures (figure 14) [60, 126]. The $\mu_0 H_0(T)$ for $H_\parallel c$ is slightly larger than the value predicted with equation (11) at low temperatures, but is smaller than the theoretical one for $H_\parallel ab$. For $H_\parallel ab$, fitting with equation (8) yields $\alpha = 5.6$ and $\lambda_0 = 0.3$, indicating that the spin-paramagnetic effect may play an important role in suppressing superconductivity for $H_\parallel ab$ [60]. On the other hand, the enhancement of $\mu_0 H_0(T)$ for $H_\parallel c$ at low temperatures may be related to the multiband effect [60]. These behaviors are very similar to those of FeAs-1111 and FeAs-122, but not FeCh-11 compounds. In $K_{0.8}Fe_{1.76}Se_2$, the $\gamma(T)$ increases with temperature and finally decreases gradually with increasing temperature. But in $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$, the $\gamma(T)$ decreases with temperature in the entire measurement range with larger values when compared to $K_{0.8}Fe_{1.76}Se_2$. Similar to other iron-based superconductors, the decrease of $\gamma(T)$ with temperature may be related to the multiband effect or to the gradual setting in of pair breaking by the spin-paramagnetic effect, which requires $\mu_0 H_{c2,ab} = \mu_0 H_{c2,c}$ in the low-temperature and high-field limit [103]. On the other hand, the $\gamma(T)$ values in $K_{0.8}Fe_{1.76}Se_2$ and $Tl_{0.58}Rb_{0.42}Fe_{1.72}Se_2$ are much larger than those in FeCh-11 materials. This difference could be related to the decrease of dimensionality when compared to FeCh-11 superconductors.

For both FeCh-11 and AFeCh-122 superconductors, doping on Fe site is usually detrimental for superconductivity [127, 128]. On the contrary, in FeAs-based superconductors doping on Fe site is beneficial as it induces superconductivity in compounds such as Ba(Fe,Co)$_2$As$_2$ [8].

In FeCh-11 materials, doping on Ch site enhances superconductivity in compounds such as Ba(Fe,Co)$_2$As$_2$ [8].

As shown in figure 15(a), the lattice parameters decrease with S doping due to the smaller ionic size of S$^{2-}$ than Se$^{2-}$. The trend of lattice contraction approximately follows the Vegard’s law. In addition, doping S into Se site does not lead to random Fe occupation of Fe1 and Fe2 sites. The refinements within single-phase 14/m crystallographic space group show that the Fe1 site has a low occupancy, whereas the Fe2 site is almost fully occupied. Besides K$_x$Fe$_{2-y}$S$_2$, all
other crystals show metallic behavior with resistivities below $\rho_{\text{max}}$ at temperatures above $T_c$ (figure 15(b)). It should be noted that the temperature of $\rho_{\text{max}}$ varies non-monotonically with the doping level of $S(z)$, implying that the temperature of the crossover may be influenced by both K and Fe deficiencies. Shoemaker et al. [130] found that the temperature dependence of resistivity in the normal state can be described well by a two-phase model containing metallic and insulating phases. This result suggests that the metal-semiconductor crossover can be partially related to the two-phase coexistence in K$_x$Fe$_{2-x}$Se$_2$, i.e. the phase separation in the samples, which has been observed by various measurement techniques [32-38]. On the other hand, the crystal with $z = 2$ is semiconducting even if the Fe deficiency is smaller than in the other samples. Whether there is also phase separation in K$_x$Fe$_{2-x}$Se$_2$ needs to be investigated in the future.

The changes in the ground state phase diagram of K$_x$Fe$_{2-x}$Se$_2$ are due to the sulfur doping and should not be influenced by the microscopic phase separation. If K$_x$Fe$_{2-x}$Se$_2$ shows superconducting behavior, the $T_c$ is always above 30 K and is never below 30 K [75]. It means that the $T_c$ is not sensitive to the compositional fluctuation of K or Fe once superconductivity appears. So, the gradual decrease of $T_c$ in K$_x$Fe$_{2-x}$Se$_2$ is difficult to ascribe to compositional fluctuations due to the phase separation. In contrast to $\rho_{\text{max}}$, the $T_c$ is monotonically suppressed to lower temperature with the increase in S and cannot be observed above 2 K for $z \geq 1.58$. The superconductivity of K$_x$Fe$_{2-x}$Se$_2$ single crystals with $z < 1.58$ is confirmed by the magnetization measurement (figure 15(c)). The Curie–Weiss temperature dependence is absent for all samples above 50 K as shown in figure 15(c). Magnetic susceptibilities are weakly temperature dependent with no significant anomalies above 50 K. This suggests the presence of low-dimensional short-range magnetic correlations and/or a long-range AFM order above 300 K. Interestingly, non-superconducting samples show bifurcation between the ZFC and FC curves for both field directions, suggesting spin glass (SG) transition at low temperatures in the 1.58 $\leq z \leq 2$ range. The magnetic and superconducting phase diagram of K$_x$Fe$_{2-x}$Se$_2$ is shown in figure 15(d). Semiconductor-metal crossover can be traced for 0 $\leq z \leq 1.58$ at high temperatures. In this $z$ region, K$_x$Fe$_{2-x}$Se$_2$ becomes a small-gap semiconductor with no metallic crossover and with a SG transition below 32 K.

The gradual changes of $T_c$ are difficult to explain only by the slight variation of Fe and K contents, because usually the superconductivity appears with higher Fe content when K content ($x$) $< 0.85$ [131, 75]. As opposed to this trend, the K$_x$Fe$_{2-x}$Se$_2$ crystals with larger $z$ values have higher Fe contents but lower $T_c$, indicating that $T_c$ is not only governed by K/Fe stoichiometry or vacancies. The local environment

![Figure 15.](image)

Figure 15. (a) Unit cell parameters as a function of S substitution. Inset: crystal structure of K$_x$Fe$_{2-x}$Se$_2$ in I4/m unit cell with vacant Fe1 sites marked light red and Fe2 sites marked dark purple. (b) Temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ of the K$_x$Fe$_{2-x}$Se$_2$ in zero field. Inset: temperature dependence of $\rho_{ab}(T)$ below 40 K for 0 $\leq z \leq 1.2$. (c) Temperature dependence of $\chi(T)$ at $\mu_0H = 0.1 \text{T}$ for $H||c$ for zero-field cooling (ZFC) and FC, respectively. (d) Magnetic and superconducting phase diagram of K$_x$Fe$_{2-x}$Se$_2$. Green, blue and orange colors show semiconducting, magnetic and superconducting phases, respectively. Red symbols denote spin glass transitions. Reprinted with permission from [68]. Copyright 2011 by the American Physical Society.
of Fe profoundly changes with S doping, inducing the changes in band structure and physical properties. In the K$_x$Fe$_{2−y}$Se$_{2−z}$S$_z$ crystal structure refined in I4/m space group, Fe atoms have block-like distribution where four Fe2 sites form a square around Se atom, making a cluster distinct from Fe1 site with low occupancy (inset of figure 15(a)) [31]. Therefore there are Fe1–Fe2 distances as well as intra- and inter-cluster Fe2–Fe2 distances. All cluster distances are unchanged with S doping whereas the Fe1–Fe2 distances decrease significantly (figure 16(a)). A similar magnetization behavior above 50 K and rather different superconducting $T_c$ values as S content varies from 0 to 2 coincide with the nearly unchanged Fe2–Fe2 bond lengths. This result shows that superconductivity is insensitive to the size of Fe2–Fe2 clusters whereas the unchanged high-temperature magnetism could be related to the unchanged Fe2–Fe2 bond lengths. On the other hand, the SG behavior arising at low temperatures for non-superconducting samples can be explained by the non-zero random occupancy of Fe1 (vacancy) site for a higher S content (figure 16(b)), randomly changing the inter-cluster exchange interactions [132].

The correlation of $T_c$ with the anion height between Fe and Pn (Ch) layers was empirically observed. There is an optimal distance ($\sim$1.38 Å) with a maximum $T_c$ $\sim$ of 55 K [133]. This seems to be invalid in K$_x$Fe$_{2−y}$Se$_{2−z}$S$_z$ materials, where there are two Fe and two Ch sites and four Fe–Ch heights. There is no monotonic decrease as $T_c$ is tuned to 0, whereas both Se and S end members have rather similar anion heights (figure 16(c)). The bond angle $\alpha$ between Pn(Ch)–Fe–Pn(Ch) is more instructive since $T_c$ in iron pnictides is optimized when Fe–Pn (Ch) tetrahedron is regular ($\alpha = 109.47^\circ$) [134]. In K$_x$Fe$_{2−y}$Se$_{2−z}$S$_z$, the Ch2–Fe1–Ch2 angle changes toward the optimal value with increasing S content (figure 16(d)), but the local environment of Fe2 site exhibits inverse trend. Among six angles in the Fe2–Ch1(2) tetrahedron, three (Ch1–Fe2–Ch2) are nearly unchanged with S doping (figure 16(e)). The other three (Ch1–Fe2–Ch1) change significantly (maximum 6°) and deviate from optimal

Figure 16. (a) Bond lengths between Fe sites. Inset shows top view of Fe layer. (b) Occupancy of Fe1 and Fe2 sites. (c) Anion height. Inset shows side view of Fe–Ch sheet. (d) Ch2–Fe1–Ch2, (e) Ch1–Fe2–Ch2 and (f) Ch2–Fe2–Ch2 bond angles of K$_x$Fe$_{2−y}$Se$_{2−z}$S$_z$ as a function of S substitution, $x$. Insets of (d–f) show Fe–Ch tetrahedron for Fe1–Ch1 and Fe2–Ch1(2). The dotted pink line in (c) shows the optimal bond lengths for $T_c$. The dotted green lines in (d–f) indicate the optimal angle for $T_c$. Reprinted with permission from [68]. Copyright 2011 by the American Physical Society.
value from Se-rich to S-rich side (figure 16(f)). Hence, the increasing distortion of Fe$_{2}$–Ch tetrahedron with S doping is closely correlated to the suppression of $T_c$. This distortion may lead to carrier localization, decreasing the density of states at the Fermi energy, which is confirmed by the measurement of thermal properties as discussed below. Therefore, the regularity of Fe$_{2}$–Ch$_{12}$ tetrahedron is an important structural factor governing the formation of the metallic states in K$_{x}$Fe$_{2y}$Se$_{2z}$S$_{x}$, and consequently the $T_c$.

Thermal properties indicate that the density of states at the Fermi energy decreases with S doping, resulting in the suppression of correlation strength [135, 136]. As shown in figure 17(a), the suppression of $T_c$ with the increase of sulfur concentration is confirmed by the shift of transition temperature where the Seebeck coefficient $S$ becomes 0 because Cooper pairs carry no entropy in the superconducting state. The diffusive Seebeck response of a Fermi liquid dominates and is expected to be linear versus temperature in the zero-temperature limit, with a magnitude proportional to the strength of electron correlations in the simple Boltzmann picture [137]. This is similar to the temperature linearity of electronic specific heat, $C_e/T = \gamma$. In a one-band system both can be described by

$$S/T = \pm \frac{\pi^2 k_B^2}{3 e} \frac{1}{T_F} = \pm \frac{\pi^2 k_B^2}{3 e} \frac{N(E_F)}{n},$$

$$\gamma_n = \frac{\pi^2 k_B^2}{3 e} \frac{n}{T_F} = \frac{\pi^2 k_B^2}{3 e} N(E_F),$$

where $e$ is the electron charge and $T_F$ is the Fermi temperature, which is related to $E_F$ and $N(E_F) = \frac{3n}{2E_F} = \frac{3n}{k_B T_F}$ [137]. For superconducting crystals, the Seebeck coefficient in the normal state is independent of magnetic field and exhibits a linear relationship with temperature which can be fitted using equation (29) very well in the low-temperature range (figure 17(a)). With S doping, $S/T$ is suppressed from $-0.48 \mu V K^{-2}$ to a very small value of $\sim 0.03 \mu V K^{-2}$ for crystals without superconducting transition. Similar to $S/T$, the electronic Sommerfeld coefficient in the normal state $\gamma_n$ is also gradually suppressed with the increase in sulfur content (inset of figure 17(b)). According to equations (29) and (30), $S/T$ and $\gamma_n$ are related to $n$ and $N(E_F)$. Since sulfur has an identical electronic configuration to selenium, there should be no simple change in the carrier concentration with sulfur doping because the elemental analysis is consistent with full occupancy of Se (S) sites [68].

The absolute value of the dimensionless ratio of the Seebeck coefficient to specific heat, $q = N_A e^2 S/T \gamma_n$, where $N_A$ is the Avogadro number, gives the carrier density $n$. The values of $q$ do not exhibit significant change [136]. Therefore, the suppressions of $S/T$ and $\gamma_n$ reflects a suppression of $N(E_F)$.

The ratio of $T_c$ to $T_F$ characterizes the correlation strength in superconductors. In unconventional superconductors, such as CeCoIn$_5$ and YBa$_2$Cu$_3$O$_{6.67}$, this ratio is about 0.1, but it is only ~0.02 in BCS superconductors, such as LuNi$_2$B$_2$C [135]. In Fe$_{1+y}$Te$_{1-x}$Se$_x$, $T_c/T_F$ it is also near 0.1, pointing to the importance of electronic correlations [138]. The ratio $T_c/T_F \sim 0.04$ for K$_{0.61}$Fe$_{1.42}$Se$_2$ implies a weakly correlated superconductor [135] when compared to Fe$_{1+y}$Te$_{1-x}$Se$_x$. A theoretical study pointed out that the ordered Fe vacancies could induce band narrowing and consequently decrease the correlation strength needed for the Mott transition [139]. With increasing sulfur content, the value of $T_c/T_F$ decreases further [136]. This implies a suppression of electron correlation strength as the system is tuned toward semiconducting states. The effective mass $m$, derived from $k_B T_F = h^2 k_F^2 / 2m$, is also suppressed with the increase in S content, consistent with the decrease of correlation strength with S doping [136].

S doping affects not only $T_c$ and properties in the normal state, but also $\mu_0 H_c^2(T)$. As shown in figure 18(a), with S doping, for K$_{0.70}$Fe$_{1.55}$Se$_{1.01}$S$_{0.99}$ (S-99), $d\mu_0 H_c^2(T)/dT|_{T=T_c}$ is 2.74(7) and 0.649(7) $T K^{-1}$ for $H || ab$ and $H || c$, respectively, and for K$_{0.70}$Fe$_{1.61}$Se$_{0.96}$S$_{1.04}$ (S-104), $d\mu_0 H_c^2(T)/dT|_{T=T_c}$ is 3.15(4) and 0.499(4) $T K^{-1}$ for $H || ab$ and $H || c$, respectively [140]. Both are much smaller than in K$_{0.61}$Fe$_{1.42}$Se$_2$ (S-0). Therefore, the $\mu_0 H_c^2(T)$ values obtained with equation (10) are significantly smaller than those in S-0 for both field directions. Using $x_{c-ph} = 0.5$, the Pauli limiting field $\mu_0 H_B(0) = 1.86T_c(1 + \kappa_{c-ph})^{1/2}$ is 53.5 and...
41.0 T for S-99 and S-104, respectively. Both values are larger than extrapolated $\mu_0 H_{c2,c}(0)$ using equation (11) for S-99 and S-104. It should be noted that for the $\mu_0 H_{c2,c}(T)$ of S-99 and S-104, there is no upturn at low temperatures when compared to undoped AFeSe-122 materials [60, 126]. Moreover, the fits using simplified WHH theory are rather satisfactory for temperatures far below $T_c$ for $H//c$ for both S doped samples. All this implies that for S-99 and S-104 the spin-paramagnetic and multiband effects are negligible when the magnetic field is applied along the $c$-axis. This is different from undoped AFeSe-122 materials [60, 126]. The changes of the $\mu_0 H_{c2,c}(T)$ with S doping could be due to the changes of band structure. Experiments in higher field and lower temperature are needed to shed more light on the behaviors of $\mu_0 H_{c2,ab}(T)$.

To characterize the evolution of the anisotropy $\gamma(T)$ with S doping near $T_c$, the angular-dependent resistivity $\rho_{ab}(\theta, \mu_0 H, T)$ is measured at various magnetic fields and temperatures, where $\theta$ is the angle between the direction of external field and the c-axis of the samples. According to the anisotropic Ginzburg–Landau (GL) model, the effective upper critical field $\mu_0 H_{c2}^{GL}(\theta)$ can be represented as [141]

$$\mu_0 H_{c2}^{GL}(\theta) = \mu_0 H_{c2,ab}/(\sin^2 \theta + \gamma^2 \cos^2 \theta)^{1/2},$$

where $\gamma = H_{c2,ab}/H_{c2,c} = (m_c/m_{ab})^{1/2} = \xi_c/\xi_e$. Since the resistivity in the mixed state depends on the effective field $H/H_{c2}^{GL}(\theta)$, the resistivity can be scaled with $H/H_{c2}^{GL}(\theta)$ and data should collapse onto one curve in different magnetic fields at a certain temperature when a proper $\gamma(T)$ value is chosen [141]. Figures 18(b)–(d) show the relation between resistivity and scaling field $\mu_0 H_c = \mu_0 H(\sin^2 \theta + \gamma^2 \cos^2 \theta)^{1/2}$ for S-0, S-99 and S-104, respectively. Good scaling is obtained by adjusting $\gamma(T)$. The temperature dependence and value of $\gamma(T)$ for S-0 (the inset of figure 18(b)) are similar to reported results [126]. For S-99 and S-104, the $\gamma(T)$ exhibits the same trend as that for S-0, i.e. increasing with temperature. However, the value increases gradually with increasing S content (figures 18(c) and (d)). It changes from $\sim 3$ for S-0 to $\sim 6$ for S-104. The larger anisotropy with increasing S content may suggest that the two-dimensional Fermi surface is becoming less warped with S doping [123].

**4.4. Spin-paramagnetic effect in iron-based superconductors**

According to equation (14), the Maki parameter $\alpha$ can be calculated as $\alpha = [(H_{c2}^s(0)/H_{c2}(0))^2 - 1]^{1/2}$. It can be also obtained from the fitting using equation (8) or (27). We summarize the $\alpha$ of iron-based superconductors reported in the literature for $H//ab$ and $H//c$ (figure 19). There are three general trends for $\alpha$: (i) $\alpha_{H//ab}$ are larger than $\alpha_{H//c}$ for all of superconductors, indicating that the spin-paramagnetic effect is weaker for $H//c$ than for $H//ab$. (ii) FeCh-11 shows the largest $\alpha$ for both field directions with $\alpha > 1$, reflecting that the spin-paramagnetic effect is the dominant pair-breaking effect.
Figure 19. Maki parameters $\alpha$ obtained from $\alpha = \{H^2(0)/H_C(0)^2\} - 1/2$ or fitting using equation (8) or (13) in various iron-based superconductors for (a) $H_{ab}$ and (b) $H_c$: $\text{Tl}_{0.35}\text{Rh}_{0.65}\text{Fe}_{1.23}\text{Se}_2$ [60], $\text{SmFeAsO}_{0.85}\text{Fe}_{1.2}$ [105], $\text{SmFeAsO}_{0.85} \text{Te}_{0.15}$ [110], $\text{Fe}_{1.02}\text{S}_0.6\text{Te}_0.4$ [110], $\text{Ba}_{0.68}\text{K}_{0.32}\text{Fe}_{2}\text{As}_2$ [117], $\text{Ba}_{0.66}\text{K}_{0.34}\text{Fe}_{2}\text{As}_2$ [122], $\text{Ba}_{0.66}\text{K}_{0.32}\text{Fe}_{2}\text{As}_2$ [144], $\text{SrFe}_{0.96}\text{Co}_{0.04}\text{As}_2$ [145], $\text{LiFeAs}$ [109], $\text{FeSe}_{0.3}\text{Te}_{0.7}$ thin film [150], $\text{Ba}_{0.66}\text{K}_{0.34}\text{Fe}_{2}\text{As}_2$ [150], $\text{Ba}_{0.66}\text{K}_{0.34}\text{Fe}_{2}\text{As}_2$ [151] and $\text{Ca}_0.9\text{Pb}_{0.1}\text{As}_6$ [152].

Figure 20. The mass enhancement $m^*/m_{\text{band}}$ of the iron 3d orbitals in the paramagnetic state, calculated with the density functional theory and cellular dynamical mean field theory (DFT+CDMFT), and the low-energy effective mass enhancement obtained from optical spectroscopy experiments and (angle-resolved) photoemission spectroscopy experiments. Reprinted with permission from [41]. Copyright 2011 by the Macmillan Publishers Ltd: Nature Mat.

On the other hand, the evolution of spin-paramagnetic effect in iron-based superconductors ($\text{FeCh-11, AFeCh-122 > FeAs-111 > FeAs-122 > FeAs-1111}$) can be partially related to the evolution of the enhancement of effective mass in these materials according to equations (15) and (16) (figure 20) [41]. Moreover, the low carrier density $n$ in iron-based superconductors [42, 43], resulting in the smaller $E_F$ according to the free electron model, will also lead to the larger $\alpha$.

We now comment on the recently discovered phase separation in $\text{K},\text{Fe}_{2-\delta}\text{Se}_2$ crystals [32–38]. Since the wide-gap semiconducting phase is locked at high temperatures, (super)conductivity originates from the volume fraction of the sample that is conducting below the high-temperature structural transition. This should not have a major effect on $\mu\beta H_C(T)$ phase diagrams, fits and estimate of mechanism of pair breaking in high fields. The values of $J_c$ could be affected to some extent because the Bean model was applied to inhomogeneous samples. Yet, due to the rather small scale of phase separation and Josephson coupling that bridges insulating nanoislands [35], values of $J_c$ represent a lower estimate of the $J_c$ and should be close to the intrinsic values for the superconducting phase. A similar argument can be applied for diffusion thermopower $S$ and conclusions based on the correlation strength in the normal state since $S$ does not depend on the sample geometry. In contrast, resistivity values represent the upper limit of $\rho$ for the superconducting phase, similar to polycrystalline samples with grain boundary contributions.

5. Conclusions

In summary, iron chalcogenide superconductors now have $T_c$ and $\mu\beta H_C$ values that are comparable to those of iron pnictide superconductors. Whereas the $J_c$ are still...
low in $K_2FeSe_2$ when compared to ternary arsenide superconductors, the $\mu_0H_{c2}$ values are in similar range. Because of the strong correlations present in the normal state and/or in the parent materials, spin-paramagnetic effects on $\mu_0H_{c2}(T)$ are significant in binary FeCh-11 superconductors, probably masking multiband evolution of $\mu_0H_{c2}(T)$. Enhanced spin-paramagnetic effects most likely originate from a Kondo-like interaction with the more localized Fe orbitals. This is in contrast to ternary AFeCh-122 materials where electronic correlations in the normal state are weaker and where much of the $\mu_0H_{c2}(T)$ and vortex behavior is still unexplored due to extremely large upper critical fields and complex structural features.

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