Topical Review

Structure, magnetic order and excitations in the 245 family of Fe-based superconductors

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Abstract
Elastic neutron scattering simultaneously probes both the crystal structure and magnetic order in a material. Inelastic neutron scattering measures phonons and magnetic excitations. Here, we review the average composition, crystal structure and magnetic order in the 245 family of Fe-based superconductors and in related insulating compounds from neutron diffraction works. A three-dimensional phase-diagram summarizes various structural, magnetic and electronic properties as a function of the sample composition. A high pressure phase diagram for the superconductor is also provided. Magnetic excitations and the theoretic Heisenberg Hamiltonian are provided for the superconductor. Issues for future works are discussed.

Keywords: Fe-based superconductors, magnetic order, magnetic excitations, phase diagram

Most Fe-based superconductors are pnictides [1]. There had been only one family of iron chalcogenide superconductors Fe$_{1+\delta}$(Se,Te) of maximum $T_C \approx 14$ K at ambient pressure [2, 3] and 37 K at high pressure [4], before a new iron chalcogenide superconductor of the nominal composition K$_{0.8}$Fe$_2$Se$_2$ was reported in 2010 with $T_C \approx 30$ K [5]. A transient transition around 40 K from a part of the sample was also reported in the work, which may be related to the superconducting transition realized later in A$_2$Fe$_2$Se$_2$(NH$_2$)$_x$(NH$_3$)$_y$ (A = K, Li) [6, 7].

The Fe$_{1+\delta}$Se (11) superconductor is made of charge neutral FeSe layers of the anti-PbO structure, with the excess Fe important to the stability of the structure [8, 9]. The weakly coupled layers are susceptible to intercalation. We will review magnetic order and excitations of the 30 K intercalated chalcogenide superconductors from neutron scattering studies. To do that, it is also necessary to review the sample composition, crystal structure and phase diagrams of the new family of Fe-based superconductors, which are causing much confusion and controversy at present due to inadequate sample characterization. The physical parameters of the five A$_2$Fe$_2$Se$_5$ (245) superconductors are summarized in table 1.

| A   | K   | Rb   | Cs   | Tl,K | Tl,Rb |
|-----|-----|------|------|------|-------|
| a (Å) | 8.7306(1) | 8.788(5) | 8.865(5) | 8.645(6) | 8.683(5) |
| c (Å) | 14.1128(4) | 14.597(2) | 15.289(3) | 14.061(3) | 14.388(5) |
| $M$ ($\mu_B$) | 3.31(2) | 3.3(1) | 3.3(1) | 3.2(1) | 3.2(1) |
| $T_C$ (K) | 32 | 32 | 29 | 28 | 32 |
| $T_N$ (K) | 559(2) | 502(2) | 471(4) | 500(1) | 511(1) |
| $T_S$ (K) | 578(2) | 515(2) | 50(01) | 533(2) | 512(4) |

**1. Sample composition and crystal structure of the superconductors**

After the initial report [5] and confirmation [12] of superconductivity in the nominal K$_{1.5}$Fe$_2$Se$_2$, Cs and Rb compounds of the similar nominal composition [13, 14] as well as Tl containing compounds of a different nominal composition (Tl,A)Fe$_2$...-xSe$_2$ (A = K,Rb) [15,16] were also reported to
superconduct at $T_C \approx 30$ K. The former composition formula indicates an intact FeSe plane, as in the 11 compounds, as well as ‘heavy electron doping’ [17]. The latter suggests Fe vacancy in the FeSe plane since two different kinds of Fe vacancy orders have been previously reported in chalcogenide TlFe$_{2-\delta}$Se$_2$ and TlFe$_{2-\delta}$P$_2$ [18, 19].

The nominal K$_{0.8}$Fe$_2$Se$_2$ and Cs$_{0.8}$Fe$_2$Se$_2$ superconducting samples used in the ARPES study to conclude a heavy electron doping [17], however, are refined to be K$_{0.775(4)}$Fe$_{1.613(1)}$Se$_2$ and Cs$_{0.748(2)}$Fe$_{1.626(1)}$Se$_2$ in the single-crystal x-ray diffraction study using the samples from the same source [20]. One superconducting sample from a systematic synthesis study of another group [21] is found to be K$_{0.737(6)}$Fe$_{1.631(3)}$Se$_2$ in the single-crystal x-ray diffraction study [20], while another superconducting sample is found to be K$_{0.832(2)}$Fe$_{1.640(1)}$Se$_2$ in a powder neutron diffraction refinement study [10]. Thus, the iron valance in the superconducting samples is very close to, but not exactly at 2+, similar to that in the previously discovered iron chalcogenide superconductors Fe$_{1+\delta}$(Se,Te) [8, 9], but very different from the conclusion of the ARPES studies which claim intact FeSe layers in A$_{0.8}$Fe$_2$Se$_2$ [17, 22, 23]. An alternative interpretation of the ARPES data has been offered by Berlijn et al. [34].

The Fe vacancy not only exists in these new superconductors but also forms a nearly ideal $\sqrt{5} \times \sqrt{5}$ superlattice on the FeSe square plane, see figure 1. The ordered structure is refined in the tetragonal $I4/m$ unit cell and the structure parameters are tabulated in [10, 20]. The prominent structural feature of the superconducting samples is the almost empty 4$d$ Fe1 site with an occupancy $n(4d)$ at a few percent and the full occupancy of the 16$i$ Fe2 site, see table 2, below room temperature.

If the Fe1 site is completely empty and the Fe2 site fully occupied with the perfect $\sqrt{5} \times \sqrt{5}$ Fe vacancy order, the sample composition would be A$_{0.8}$Fe$_{1.6}$Se$_2$, or A$_2$Fe$_4$(Se,Te) (245). As the non-stoichiometric Fe$_{1+\delta}$(Se,Te) (11) superconductors are referred to as the 11 family, the slightly off-stoichiometric iron selenide superconductors with the Fe vacancy order A$_{2-\delta}$Fe$_{4+\delta}$Se$_5$, where $4\delta = n(4d)$ and $\epsilon \sim 2\delta$ due to the Fe valence $\sim 2+$, can also be referred to as the 245 superconductors [10, 20].

In addition to K and Cs, the A = Rb, (Tl,K) and (Tl,Rb) superconducting A$_2$Fe$_4$Se$_5$ samples also possess the same nearly ideal $\sqrt{5} \times \sqrt{5}$ Fe vacancy order [11]. The Fe vacancy order in all of these five known 245 superconductors disappears in an order-disorder structural transition at a very high temperature $T_S$, ranging from 500 to 578 K, respectively [10, 11].

Above the transition at $T_S$, the Fe1 and Fe2 sites become equally occupied, thus restoring the $I4/m$mm symmetry as in the BaFe$_2$As$_2$ (1 2 2) system. However, it should be noted that this high-temperature compound cannot be called AFe$_2$Se$_2$ as many people have mistakenly done in current literature, since the occupancy at the Fe and A sites in the $I4/m$mm structure is only around 0.8 in these superconductors, see table 2 in [10]. The sample composition remains close to A$_{0.8}$Fe$_{1.6}$Se$_2$, i.e. 245. In other words, 245 does not always have the $\sqrt{5} \times \sqrt{5}$ superlattice structure. Temperature is one determining factor, one can see more on this point in the phase-diagram section.

A 245 compound at a high temperature above $T_S$ does not make it a 122 compound, despite its share of the same space group symmetry $I4/m$m with the 122 compounds.

2. Magnetic order of the 245 superconductors

Slightly below the order-disorder transition $T_S = 578$ K, an antiferromagnetic order develops at $T_N = 559$ K in the K$_2$Fe$_4$Se$_5$ superconductor [10]. The $c$-axis is the easy axis of the magnetic order. The four magnetic moments on the nearest-neighbour square block behave like a superspin, forming the simple chessboard antiferromagnetic pattern in the plane, see figure 2. With the development of the staggered magnetic moment which reaches 3.3(1) $\mu_B$/Fe at 11 K, the distance between the four Fe atoms on the block of the same spin orientation also shrinks from the regular square lattice in the high temperature $I4/m$m structure [10]. This strong magnetostructural tetramerization greatly contributes to the stability of the block antiferromagnetic order on the $\sqrt{5} \times \sqrt{5}$ vacancy ordered lattice according to band structure calculations [27, 28].

The same large moment and high $T_N$ antiferromagnetic order in figure 2 also exists in the remaining four 245 superconductors [11]. In figure 3(a), magnetic Bragg peak (1 0 3) due to the tetramer block antiferromagnetic order is shown as a function of temperature together with the structural Bragg peak (1 1 8) due to the $\sqrt{5} \times \sqrt{5}$ Fe vacancy order. The magnetic order starts to develop as soon as sufficient order has been established in the $\sqrt{5} \times \sqrt{5}$ superlattice. Figure 3(b) compares the squared magnetic order parameter of the five 245 superconductors. The $T_N$ ranges from 471 to 559 K but the staggered magnetic moment stays at 3.3(1) $\mu_B$/Fe, close to the atomic value 4 $\mu_B$/Fe for the Fe$^{2+}$ ions, refer to table 1. The staggered magnetic moment in 245 superconductors is...
Table 2. Occupancy at the minority Fe1 site 4d and majority Fe2 site 16i at various temperatures for the superconducting sample K_{0.83}Fe_{1.64}Se_{2} and the insulating samples K_{0.93}Fe_{1.52}Se_{2}, K_{0.86}Fe_{1.56}Se_{2} and K_{0.99}Fe_{1.48}Se_{2}. The quantity 1 − n(4d)/n(16i) can serve as a measure for the perfectness of the √ 5 × √ 5 vacancy order.

| T (K) | K_{0.83}(2)Fe_{1.64}Se_{2} [10] | K_{0.86}(2)Fe_{1.56}Se_{2} [25] | K_{0.91}(1)Fe_{1.52}Se_{2} [25] | K_{0.99}(1)Fe_{1.48}Se_{2} [26] |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 11    |                                 |                                 |                                 |                                 |
| 295   |                                 |                                 |                                 |                                 |
| 500   |                                 |                                 |                                 |                                 |
| 550   |                                 |                                 |                                 |                                 |
| 90    |                                 |                                 |                                 |                                 |
| 100   |                                 |                                 |                                 |                                 |
| 295   |                                 |                                 |                                 |                                 |

![Figure 2](image)

Figure 2. (a) Magnetic structure of K_{2}Fe_{2}Se_{5} in the I4/m unit cell. (b) The in-plane antiferromagnetic ordering pattern of the four-spin blocks is highlighted with the two different colors which represent the alternating moment directions along the c-axis (reproduced from [10]).

larger than the record size 2.0 μ_B/Fe of previous Fe-based superconductors [8].

One remarkable feature of the 245 superconductors is the coexistence of superconductivity with the very strong antiferromagnetic order. The inset of figure 3 shows the inflection of the magnetic intensity when T_C is approached in a (Tl,Rb)_2Fe_2Se_5 superconductor. This indicates strong interaction between the antiferromagnetic order and superconductivity and has served as definite evidence of the coexistence in unconventional magnetic superconductors, such as heavy-fermion UPt_3 [29] and Fe-based Ba(Fe_{0.93}Co_{0.07})_2As_2 [30]. The superconducting symmetry of the 245 materials has to be such that it can survive in the tremendously strong staggered magnetic field imposed by the large magnetic moment.

While the antiferromagnetic order in 245 superconductors does not break the four-fold tetragonal crystal symmetry, antiferromagnetic order in all previous families of Fe-based superconductors exists in a distorted crystal structure of a symmetry lower than the tetragonal one [8, 31, 32]. It has been discovered in works of neutron diffraction that there are empirical rules that define the relation between the shortened spacing of the Fe neighbouring pair and their ferromagnetic interaction and the relation between the expanded spacing and antiferromagnetic interaction in NdFeAsO (1111) [33], BaFe_2As_2 [32] and Fe_{1+}Te [8] of the 1111, 122 and 11 families. This intimate structure-magnetism relationship can be explained as being due to different occupancies of the d_{xz} and d_{yz} orbitals, which leads to the structural distortion from the in-plane four-fold symmetry and prepares the magnetic exchange interactions of correct signs for the observed antiferromagnetic order [8, 32–34]. Such an orbital ordering mechanism can also be successfully applied to explain the tetramer block antiferromagnetism in 245 superconductors in a unified fashion [35, 36], satisfying the same empirical rules connecting the lattice expansion (contraction) with (anti)ferromagnetic exchange interaction [10]. Meanwhile, the spin-density-wave scenario due to the nesting Fermi surface [31] faces serious experimental difficulties, such as the lack of an anomaly in resistivity at T_N. Refer to [37] for more detailed discussion.

When the lattice distortion of Fe_{1+}Te is suppressed with Se substitution, the long-range antiferromagnetic order that breaks the four-fold symmetry is replaced by a glassy short-range magnetic order [8]. Figure 4 shows the diffuse scattering pattern in the basal plane from the glassy order. The order
contains the same tetramer block of 245 superconductors as a constituent in fluctuating magnetic clusters [38, 39]. Thus, it appears that the magnetostructural tetramerization is a common tendency among the two families of iron chalcogenide superconductors [36]. The condensation of the tendency to a long-range order possibly needs the relief of magnetic frustration that is alluded to by Yildirim [34], with the lattice distortion in the 11 family or the tetramerization introduced by the $\sqrt{3} \times \sqrt{3}$ vacancy order in the 245 family.

3. Composition phase diagram

No polycrystalline 245 superconductor has been reported so far. The grown single crystal is also usually non-superconducting. The crystal becomes superconducting after an annealing process. When the superconducting sample is ground for powder diffraction experiments, we always find pure Fe intergrowth between the 245 plates [10]. This may not be surprising for intercalating compounds. However, it has contributed to widespread systematic error in the determination of the sample composition in current research, which derives the nominal composition either by using the starting material ratio, or by employing the inductively coupled plasma (ICP) analysis method when both the genuine 245 crystal and the Fe intergrowth are vaporized. In neutrons or x-ray diffraction experiments, different materials in the bulk sample can be detected and their compositions and structures separately refined. We have found that the refined composition is quite different from the nominal composition [10, 20].

Figure 5 shows the phase diagram of $K_xFe_{2-x}Se_2$, of which samples were prepared using the same procedure for the series of samples published in [21]. First of all, the $x$ and $y$ in the chemical formula $K_xFe_{2-x}Se_2$ are not completely independent and the actual sample compositions are shown on the basal plane cluster along the black line $x = 2y$ which defines the Fe valence exactly at 2+. Thus, the series of samples made using the Bridgman method all contain Fe of valence close to 2+. Consequently, with $x \approx 2y$, the charge neutrality requires that when more K of valence 1+ is intercalated between the FeSe planes, more Fe vacancy is created. When $x = 0.8$ and $y = 0.4$ ($2y = 1.6$) at the left side of the phase-diagram, $K_xFe_{2-y}Se_2$ becomes $K_{0.8}Fe_{1.6}Se_2$, namely $K_2Fe_3Se_5$. One of five Fe sites is vacant. When $x = 1$ and $y = 0.5$ at the right, $K_xFe_{2-y}Se_2$ is $KFe_5Se_2$, i.e. $K_2Fe_3Se_5$ (234). One of four Fe sites is vacant.

The two superconducting samples on the left in the phase diagram figure 5 show a consistently high resistivity above $T_C$, see figure 6(a). They also show a poor diamagnetic response below $T_C$, see the inset to figure 6(c). Moving to the right in the phase diagram, the normal state resistivity of the next three superconducting samples show a bump, which defines the metal-insulator crossover point (blue triangle and dashed line) in the phase diagram. These samples demonstrate a much better diamagnetic response. The sample $K_{0.43}Fe_{1.64}Se_2$ of the highest crossover temperature, showing the lowest overall normal state resistivity, was made following the same recipe as that used in the previous neutron powder diffraction study [10]. Below the crossover temperature where the metal-like positive-slope resistivity exists, the occupancy ratio of the two Fe sites $n(4d)/n(16f) \approx 0.06$ has approached the minimum value that we have observed, see table 2, indicating a highly ordered $\sqrt{3} \times \sqrt{3}$ vacancy superlattice.
is substantial disorder in the superconducting phase underneath [26].

except under the small dome of the metallic crossover and regions of the phase diagram stay in the insulating phase, x-ray refinement study of K$_0$Fe$_{1-x}$Se$_2$ samples, showing antiferromagnetic transition at $T_N$ and the disappearance of the one-out-of-four orthorhombic Fe vacancy order at $T^*$ (reproduced from [26]).

Moving further to the right in the phase diagram figure 5, the three insulating samples show a progressive opening of a transport activation gap from a logarithmic behaviour at low temperature, see figure 6(b) and the inset therein. Most regions of the phase diagram stay in the insulating phase, except under the small dome of the metallic crossover and the superconducting phase underneath [26].

Basca et al were the first to perform a single crystal x-ray refinement study of K$_0$Fe$_{1-x}$Se$_2$ at 90 K and K$_{0.99}$Fe$_{1.52}$Se$_2$ at 100 K [25] in this insulating phase and their compositions are marked by the crosses in the basal plane of figure 5. The crystal structure in the temperature range is described by the $I4/m$ space group. However, there is substantial disorder in the $\sqrt{5} \times \sqrt{5}$ superstructure. The refined structure parameters for the first crystal are listed in table 1 in [25]. The occupancy at the two Fe sites is quoted in table 2. The $n(4d)/n(16i)$ is 0.247(3) for the first crystal and 0.129(8) for the second crystal.

We performed a neutron powder diffraction study in a wide temperature range for K$_{0.99}$Fe$_{1.48}$Se$_2$, which is very close to the 234 end member [26]. One of the four Fe is vacant at the 234 composition and the vacancy order shown in figures 7(c1) or (c2) has been discussed in works on TlFe$_2$As$_2$ and TlFe$_{1.52}$Se$_2$ [18]. Surprisingly, this orthorhombic superstructure is not the ground state in KFe$_{1.5}$Se$_2$. It appears in the order-disorder transition at $T_S \approx 500$ K down to a finite temperature $T^* \approx 295$ K as a competing phase coexisting with an imperfect $\sqrt{5} \times \sqrt{5}$ Fe vacancy order, as well as with a remnant vacancy-disordered phase of the $I4/mmm$ symmetry from a high temperature [26]. As one of the three phases in the phase separated region in the phase diagram figure 5, substantial structural faults exist in this vacancy order so that the average pattern in figure 7(c) describes our data. The refined structural parameters in the orthorhombic $Pmma$ space group are listed in table 3 in [26]. Magnetic structure in the orthorhombic phase is the same as that in the BaFe$_2$As$_2$ with the staggered moment 2.8(1) $\mu_B$/Fe from the neutron diffraction study on K$_{0.85}$Fe$_{1.45}$Se$_2$ [41].

Below 380 K, no remnant $I4/mmm$ phase can be detected in K$_{0.90}$Fe$_{1.46}$Se$_2$. Below $T^* \approx 295$ K, the $Pmma$ phase also disappears, leaving the $\sqrt{5} \times \sqrt{5}$ Fe vacancy order as the only phase at low temperature [26], consistent with the case of K$_{0.93}$Fe$_{1.52}$Se$_2$ at 100 K and K$_{0.86}$Fe$_{1.56}$Se$_2$ at 90 K in the x-ray work [25]. Refined structure parameters for K$_{0.90}$Fe$_{1.48}$Se$_2$ at 50 and 295 K are listed in table 2 of [26] and the staggered antiferromagnetic moment is 3.16(5) $\mu_B$ F$^{-1}$, similar to the value in 245 [10]. The Fe occupancy data for K$_{0.90}$Fe$_{1.46}$Se$_2$ are also quoted in table 2. Together with the data from Basca et al [25], the enhanced $n(4d)/n(16i)$ in the insulating phase of figure 5 reflects the increasing disorder necessary to resolve the mismatch between the number of Fe vacancies in the material and the number of vacancies in the $\sqrt{5} \times \sqrt{5}$ superlattice pattern.

The site disorder registered in the substantial $n(4d)/n(16i)$ value for samples away from 245 on the right part of the phase diagram in figure 5 manifests in the telltale logarithmic

![Figure 6](image-url)

**Figure 6.** The resistivity of (a) superconducting and (b) insulating K$_0$Fe$_{1-x}$Se$_2$ samples. The inset to (b) is the activation gap in transport, which closes at low temperature when $x$ is reduced to 0.86. The magnetic susceptibility of (c) the superconducting and (d) the insulating samples, showing antiferromagnetic transition at $T_N$ and the disappearance of the one-out-of-four orthorhombic Fe vacancy order at $T^*$ (reproduced from [26]).
resistivity close to the metal-insulator crossover shown in figure 6(b). Above the crossover the temperature of the 245 sample, the n(4d)/n(16i) value, also increases substantially from the 0.06 base value, see table 2. Therefore, the metal-insulator crossover in the KFe$_2$Se$_2$, K$_2$Fe$_4$Se$_5$, or K$_2$Fe$_3$Se$_4$, respectively. The vacancy order in (c) is an average of those in (c1) and (c2) (reproduced from [26]).

A phase diagram with samples scattering along a bending line on the basal plane of figure 5 has also been published and is consistent with our result [43]. However, only $T_S$, $T_N$ and $T_C$ are marked, using features in bulk measurement data at the structural and magnetic transitions identified in our neutron scattering works. The use of the valence as the x-axis in their two-dimensional phase diagram is misleading, since a valence change originating at e.g. 234 will not lead to superconductivity.

The phase separated region between $T_S$ and $T^*$ in the phase diagram figure 5 covers the room temperature. Many studies on 245 superconductors reporting phase separation used samples of actual compositions in this miscibility gap. Therefore, all of the three types of structural phases in the phase region have been observed in a transmission electron microscopy study [44]. The existence of the $\sqrt{2} \times \sqrt{2}$ Fe vacancy order also shows up in new phonon modes detected in optic and Raman measurements of various samples over the phase-diagram [45, 46].

4. Magnetic excitations of the 245 superconductors

The whole magnetic excitation spectrum in the (Tl,Rb)$_2$Fe$_4$Se$_5$ superconductor ($T_C \approx 32$ K) has been measured up to 300 meV with a chopper inelastic neutron spectrometer [42]. Some of the data is shown in figure 8, demonstrating the evolution of the spin-wave cones at the two sets of magnetic Bragg spots from a twinned single-crystal sample.

Consistent with the expectation for a large-moment antiferromagnet, a magnetic excitation spectrum can be fitted by a Heisenberg Hamiltonian of localized magnetic moments

$$H = \sum_{i,j} J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j - \Delta \sum_i S_{iz}^2, \quad (1)$$

Figure 7. An Fe layer in the (a) $I4/mmm$, (b) $I4/m$ and (c) $Pmna$ structure, respectively, with the solid line marking the unit cell. With the perfect order shown in (a) and (b) or (c), the sample composition would be KFe$_2$Se$_2$, K$_2$Fe$_4$Se$_5$, or K$_2$Fe$_3$Se$_4$, respectively. The vacancy order in (c) is an average of those in (c1) and (c2) (reproduced from [26]).
which includes five exchange constants \( J_1, J_2, J_1', J_2' \) and \( J_s \) as depicted in figures 9(a) and (b) and the single-ion anisotropy constant \( \Delta \) that quantifies the observed Fe spin \( S = 3.2(1) \) alignment along the \( c \)-axis [11]. The spin-wave dispersion, as well as the scattering intensity of the acoustic branch, can be accounted for with the following parameters [42]:

\[
\begin{align*}
S & J_1 = -30(1) \text{meV}, S J_1' = 31(13) \text{meV}, \\
S & J_2 = 10(2) \text{meV}, S J_2' = 29(6) \text{meV}, \\
S & J_c = 0.8(1) \text{meV}, S \Delta = 0.3(1) \text{meV}. \\
\end{align*}
\]

These terms help to stabilize the observed block antiferromagnetic order, except the weaker antiferromagnetic \( J_2 \) which frustrates the ferromagnetically aligned spin block. There is a qualitative agreement between these experimental values and \textit{ab initio} linear response theoretical results [47]. The resulting spin wave dispersion curves in various high symmetry directions are shown in figure 9(c).

Low energy magnetic excitations (\( \lesssim 30 \text{meV} \)) from a superconducting \( \text{Rb}_{0.83}\text{Fe}_{1.68}\text{Se}_2 \) sample has also been investigated with a chopper inelastic neutron spectrometer [48]. The data is not sufficient to determine the magnetic exchange interactions on the \( \sqrt{5} \times \sqrt{5} \) Fe vacancy lattice and the work was focused on some extra features around the in-plane \((\pi, 0)\) point in the \( 14/m \) mm unit cell notation. No such features are observed in our study on the \((\text{Tl,Rb})_2\text{Fe}_2\text{Se}_5\) superconductor. Judging from the phase-diagram in figure 5 and the fact that the magnetic zone centre of the \( Pmna \) phase is at \((\pi, 0)\) [41], the \( \text{Rb}_{0.83}\text{Fe}_{1.68}\text{Se}_2 \) sample used in the work is not likely to be pure and the \( Pmna \) impurity phase contributes the extra magnetic excitations.

The acoustic branch of the magnetic excitations (\( \lesssim 80 \text{meV} \)) from the \( \text{K}_2\text{Fe}_3\text{Se}_5 \) superconductor was measured with a triple-axis spectrometer along two directions in the reciprocal space [49]. An independent determination of the magnetic Hamiltonian, however, is out of reach. Thus, the \( J_1 \) and \( J_2 \) used in the data fitting were borrowed from the values of a neutron scattering study on an insulating \( \text{Rb}_{0.98}\text{Fe}_{1.58}\text{Se}_2 \) sample [50]. This insulating sample is located at the right side of the phase diagram, see figure 5 and thus necessarily contains substantial site disorder with a large \( n(4d)/n(16d) \) value. Although an exchange-interaction between the third nearest neighbour spin pair \( J_3 \) in the plane is possible in principle [50] in this insulating sample of rather disordered \( \sqrt{5} \times \sqrt{5} \) superlattice, the argument to include \( J_3 \) in the intensity fitting could be nullified due to the inclusion of the scattering intensity from the close-by twin Bragg spot in the coarse spatial resolution volume of the spectrometer used in the study.

We do not review inelastic neutron scattering works on the so-called ‘resonance mode’ in the 245 family of Fe-based superconductors. As shown in e.g. figure 3 of [51], for a related FeSe superconductor, the mode keeps decreasing above the superconducting transition \( T_C \). This is fundamentally different from the resonance mode, observed with significant signal to noise ratio, in the 122 family of Fe-based superconductors. The association of the spectral feature with superconductivity is premature at the moment.

5. Phase diagram at high pressure

The stoichiometric \( \text{A}_2\text{Fe}_3\text{Se}_5 \) is an antiferromagnetic semiconductor according to band structure calculations [27, 28]. Superconducting samples, as presented above, are slightly off-stoichiometric and show a metal-like transport property below the semiconductor-metal crossover temperature, figure 6(a). The 245 superconductor also locates close to the miscibility gap of the phase separation, refer to figure 5. Thus, an important question is whether the 245...
Figure 9. (a, b) Schematic diagram showing \( J_c \), the exchange interaction between spins in adjacent Fe planes and the four unique in-plane exchange interactions considered in this work. (c) Theoretical spin wave dispersions calculated using experimentally determined parameters (reproduced from [42], copyright 2013 by The American Physical Society).

superconductor is a doped semiconductor or only a minority phase in the phase-separated sample is superconducting [53]. A closely related question is whether inhomogeneity is intrinsic to an off-stoichiometric superconductor or a pure superconducting phase can be identified and hopefully isolated [44, 54–60]. The majority view at the moment is that the \( I4/m \) phase with the \( \sqrt{5} \times \sqrt{5} \) Fe superlattice and the large-moment antiferromagnetic order is irrelevant to the superconductivity. The \( A_2\text{Fe}_3\text{Se}_4 \), \( A\text{Fe}_2\text{Se}_2 \) or \( \text{A}_x\text{Fe}_2\text{Se}_2 \) phases have all been proposed as the superconducting phase.

While the samples of the 245 family of superconductors involves complex preparation issues due to the proximity to the miscibility gap, high pressure offers another way to control the phases and investigate physics properties of the material [61, 62]. In particular, superconductivity in \((\text{Tl},\text{Rb})_2\text{Fe}_4\text{Se}_5\) is suppressed by high pressure at \( P_c \sim 9 \) GPa and then reappears between 11 and 13 GPa with a higher \( T_C \approx 48 \) K [52], figure 10.

A single-crystal high pressure neutron diffraction study on the \((\text{Tl},\text{Rb})_2\text{Fe}_4\text{Se}_5\) superconductor was recently performed [63]. Both the \( \sqrt{5} \times \sqrt{5} \) Fe vacancy order and the block antiferromagnetic order can be simultaneously measured. The phase diagram is shown in figure 11. A note of caution is that a neutron scattering experiment at 9 GPa cannot be conducted at very low temperatures at this time. A close relation of the structural and magnetic orders with the superconducting phase can be deduced.

High pressure x-ray structure studies of the 245 superconductors have previously been conducted. The neutron diffraction result is consistent with that of Guo et al [61], but fundamentally different from that of Ksenofontov et al [64]. Ksenofontov et al also reported that the \( A_x\text{Fe}_2\text{Se}_2 \) phase survives beyond the pressure \( P_c \) that suppresses the superconducting phase [64].

6. Concluding remarks

Elastic and inelastic neutron scattering studies play a crucial role in determining the sample composition, crystal
structure, phase diagram, magnetic order and excitations in the 245 family of Fe-based superconductors. The well-ordered $\sqrt{5} \times \sqrt{5}$ superlattice characterized by a small $n(4d)/n(16i) \approx 0.06$ value in the $I4/m$ structure is linked with the metal-like normal state transport property, which precedes the occurrence of the superconductivity. Similar to the 11 family of iron chalcogenide superconductors, the Anderson localization of conducting electrons by disordered scattering is also fatal to superconductivity in the 245 family of iron chalcogenide superconductors.

The large-moment block antiferromagnetic order is crucial for the stability of the $\sqrt{5} \times \sqrt{5}$ Fe vacancy order over its competing phase, such as in the orthorhombic vacancy order or the disordered Fe partial occupancy in the $I4/mmm$ structure, which exists only in an intermediate temperature range. This is due to the large energy gain in the tetramerization process. The same kind of magnetostructural coupling, in which the contraction and expansion of the lattice are linked with ferromagnetic and antiferromagnetic exchange interactions, respectively, is universal in all Fe based superconducting families, reflecting the common $d$ orbital ordering mechanism.

The low charge density left after the majority of $d$ electrons form the large magnetic moment close to the atomic limit on Fe$^{2+}$, the off-stoichiometric composition of the superconducting phase and the close-by miscibility gap of multiple phases have caused complex material control and characterization issues. Whether the 245 superconductors exist as a pure phase like in e.g. the heavy fermion superconductors, or in an inhomogeneous matrix like in the cuprate superconductors, is an open question. The studies at high pressure suggest a symbiotic relation of the $\sqrt{5} \times \sqrt{5}$ vacancy order and the block antiferromagnetic order with the superconductivity.

Nonetheless, we know that the 245 superconductors are of a spin-singlet state as shown in the NMR study [65]. The superconductivity exists in close proximity with the strong antiferromagnetic order as demonstrated by its strong effect on the magnetic order parameter. Conversely, the superconducting order parameter in the 245 materials should be able to withstand the strong staggered magnetic field. Additionally, the energy gap on the Fermi surface can be measured with ARPES. Further progress in pinning down the microscopic material phase of the 245 superconductors at the correct average composition region on the phase diagram demands careful experimental study of well controlled and characterized samples.

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References

[1] Ishida K, Nakai Y and Hosono H 2009 J. Phys. Soc. Japan 78 062001
[2] Hsu F-C et al 2008 Proc. Natl Acad. Sci. 105 14262
[3] Fang M, Pham H, Qian B, Liu T, Vehstedt E K, Liu Y, Spinu L and Mao Z Q 2008 Phys. Rev. B 78 224503
[4] Medvedev S et al 2009 Nat. Mater. 8 630
[5] Guo J, Jin S, Wang G, Wang S, Zhu K, Zhou T, He M and Chen X 2010 Phys. Rev. B 82 180520
[6] Ying T, Chen X, Wang G, Jin S, Lai X, Zhou T, Zhang H, Shen S and Wang W 2013 J. Am. Chem. Soc. 135 2951
[7] Burrard-Lucas M et al 2013 Nat. Mater. 12 15
[8] Bao W et al 2009 Phys. Rev. Lett. 102 247001
[9] McQueen T M et al 2009 Phys. Rev. B 79 014522
[10] Bao W, Huang Q, Chen G F, Green M A, Wang D M, He J B, Wang X Q and Qiu Y 2011 Chin. Phys. Lett. 28 086104
[11] Ye F, Chi S, Bao W, Wang X F, Ying J J, Chen X H, Wang H D, Dong C H and Fang M H 2011 Phys. Rev. Lett. 107 137003
[12] Mizuguchi Y, Takeya H, Kawasaki Y, Oraki T, Tsadai S, Yamaguchi T and Takano Y 2011 Appl. Phys. Lett. 98 042511
[13] Krztom-Maziopa A, Shermandini Z, Pomiakushina E, Pomjakushin V, Bendele M, Amato A, Khasanov R, Luetkens H and Conder K 2011 J. Phys.: Condens. Matter. 23 052203
[14] Wang A F et al 2011 Phys. Rev. B 83 060512
[15] Fang M, Wang H, Dong C, Li Z, Feng C, Chen J and Yuan H 2011 Europhys. Lett. 94 27009
[16] Wang H, Dong C, Li Z, Zhu S, Mao Q, Feng C, Yuan H Q and Fang M 2011 Europhys. Lett. 93 47004
[17] Zhang Y et al 2011 Nat. Mater. 10 273
[18] Sabrowsky H, Roshenbergen M, Welz D, Deeppe P and Schafer W 1986 J. Magn. Magn. Mater. 54–57 1497
[19] Haggström L, Verma H R, Bjarnan S and Wäppling R 1986 J. Solid State Chem. 63 401
[20] Zavalić P et al 2011 Phys. Rev. B 83 132509
[21] Wang D M, He J B, Xia T L and Chen G F 2011 Phys. Rev. B 83 132502
[22] Mou D et al 2011 Phys. Rev. Lett. 106 107001
[23] Wang X-P, Qian T, Richard P, Zhang P, Dong J, Wang H-D, Dong C-H, Fang M-H and Ding H 2011 Europhys. Lett. 93 57001
[24] Berlijn T, Hirschfeld P J and Ku W 2012 Phys. Rev. Lett. 109 147003
[25] Bacsa J, Ganin A, Takabayashi Y, Christensen K, Prassides K, Rosseinsky M and Claridge J 2011 Chem. Sci. 2 1054
[26] Bao W, Li G N, Huang Q, Chen G F, He J B, Green M A, Qiu Y, Wang D M, Luo J L and Wu M M 2013 Chin. Phys. Lett. 30 027402
[27] Cao C and Dai J 2011 Phys. Rev. Lett. 107 056401
[28] Yan X-W, Gao M, Lu Z-Y and Xiang T 2011 Phys. Rev. Lett. 107 057001
[29] Pratt D K, Tian W, Kreyssig A, Zarestky J L, Nandi S, Ni N, Aeppli G, Bucher E, Broholm C, Kjems J K, Baumann J and Phys. Rev. Lett. 108 101 057010
[30] Luo X G, Li J Q, Hu J and Chen X H 2012 Sci. Rep. 2 212
[31] Qiu Y, Wang D M, Luo J L and Wu M M 2013 Phys. Rev. Lett. 107 216403
[32] Liu T et al 2011 Nat. Mater. 10 716
[33] Zhao J, Cao H, Borel-Courchesne E, Lee D-H and Birgeneau R J 2012 Phys. Rev. Lett. 109 267003
[34] Chi S, Ye F, Bao W, Fang M, Wang H D, Dong C H, Savici A T, Granroth G E, Stone M B and Fishman R S 2013 Phys. Rev. B 87 100501
[35] Yan Y J, Zhang M, Wang A F, Ying J J, Li Z Y, Qin W, Luo X G, Li J Q, Hu J and Chen X H 2012 Sci. Rep. 2 212
[36] Wang Z, Song Y J, Shi H L, Wang Z, Chen Z, Tian H F, Chen G F, Guo J, Yang H X and Li J Q 2011 Phys. Rev. B 83 140505
[37] Chen Z G, Yuan R H, Dong T, Xu G, Shi Y G, Zheng P, Luo J L, Guo J G, Chen X L and Wang N L 2011 Phys. Rev. B 83 220507
[38] Zhang A M, Xiao J H, He J B, Wang D M, Chen G F and Zhang Q M 2012 Phys. Rev. B 85 024518
[39] Ke L, van Schilfgaarde M and Antropov V 2012 Phys. Rev. B 86 020402
[40] Wang M, Li C, Abernathy D L, Song Y, Carr S V, Lu X, Li S, Yamani Z, Hu J, Xiang T and Dai P 2012 Phys. Rev. B 86 024502
[41] Wang M, Li C, Xiong L, He J B, Song Y, Carr S V, Lu X, Li S, Yamani Z, Hu J, Xiang T and Dai P 2012 Phys. Rev. B 86 024502
[42] Xiao Y et al 2013 Phys. Rev. B 87 140408
[43] Wang M et al 2011 Nat. Commun. 2 580
[44] Taylor A E, Sedlmaier S J, Cassidy S J, Clarke S J and Boothroyd A T 2013 Phys. Rev. B 87 220508
[45] Sun L et al 2012 Nature 483 67
[46] Shoemaker D P, Chung D Y, Clark H, Francisco M C, Avci S, Llobet A and Kanatzidis M G 2012 Phys. Rev. B 86 184511
[47] Ricci A et al 2011 Phys. Rev. B 84 060511
[48] Liu Y, Xing Q, Dennis K W, McCallum R W and Lograsso T A 2012 Phys. Rev. B 86 144507
[49] Charnukha A et al 2012 Phys. Rev. Lett. 109 017003
[50] Wang C N et al 2012 Phys. Rev. B 85 214503
[51] Ksenofontov V, Wortmann G, Medvedev S A, Tsurkan V, Deisenhofer J, Loidl A and Felser C 2011 Phys. Rev. B 84 180508
[52] Zhang A M, Xia T L, Liu K, Tong W, Yang Z R and Zhang Q M 2013 Sci. Rep. 3 1216
[53] Texier Y, Deisenhofer J, Tsurkan V, Loidl A, Inosov D S, Frei mel G and Bobroff J 2012 Phys. Rev. Lett. 108 237002
[54] Guo J et al 2012 Phys. Rev. Lett. 108 197001
[55] Gooch M, Lv B, Deng L Z, Muramatsu T, Mecn J, Xue Y Y, Lorenz B and Chu C W 2011 Phys. Rev. B 84 184517
[56] Ye F et al 2014 Chin. Phys. Lett. 31 127401
[57] Ksenofontov V, Medvedev S A, Schoop L M, Wortmann G, Palasyuk T, Tsurkan V, Deisenhofer J, Loidl A and Felser C 2012 Phys. Rev. B 85 214519
[58] Yu W, Ma L, He J B, Wang D M, Xia T L, Chen G F and Bao W 2011 Phys. Rev. Lett. 106 197001