Physics picture from neutron scattering study on Fe-based superconductors

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Neutron scattering, with its ability to measure the crystal structure, the magnetic order, and the structural and magnetic excitations, plays an active role in investigating various families of Fe-based high-$T_c$ superconductors. Three different types of antiferromagnetic orders have been discovered in the Fe plane, but two of them cannot be explained by the spin-density-wave (SDW) mechanism of nesting Fermi surfaces. Noticing the close relation between antiferromagnetic order and lattice distortion in orbital ordering from previous studies on manganites and other oxides, we have advocated orbital ordering as the underlying common mechanism for the structural and antiferromagnetic transitions in the 1111, 122 and 11 parent compounds. We observe the coexistence of antiferromagnetic order and superconductivity in the (Ba,K)Fe$_2$As$_2$ system, when its phase separation is generally accepted. Optimal $T_c$ is proposed to be controlled by the local FeAs$_4$ tetrahedron from our investigation on the 1111 materials. The Bloch phase coherence of the Fermi liquid is found crucial to the occurrence of bulk superconductivity in iron chalcogenides of both the 11 and the 245 families. Iron chalcogenides carry a larger staggered magnetic moment ($>2\mu_B$/Fe) than that in iron pnictides ($<1\mu_B$/Fe) in the antiferromagnetic order. Normal state magnetic excitations in the 11 superconductor are of the itinerant nature while in the 245 superconductor the spin-waves of localized moments. The observation of superconducting resonance peak provides a crucial piece of information in current deliberation of the pairing symmetry in Fe-based superconductors.

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I. INTRODUCTION

In 2008, the research group led by Hosono reported the discovery of superconductivity at 26 K in LaFeAs(O,F) (Kamihara et al., 2008) after having discovered superconductivity below 4 K in isostructural LaFeP(O,F) (Kamihara et al., 2006) and LaNiP(O,F) (Watanabe et al., 2007). Superconductivity at comparable $T_c$ has been reported in YNiBC (Nagarajan et al., 1994) and related materials (Cava et al., 1994) of a laminar crystal structure similar to LaFeAsO (Siegrist et al., 1994) in 1990s. Upon replacing the nonmagnetic Y by magnetic rare-earth elements, $T_c$ of these borocarbide superconductors is suppressed in accordance to the expectation for the phonon-mediated $s$-wave superconductors (Canfield et al., 1998). When La is replaced by magnetic Sm or Ce in the LaFeAs(O,F) superconductor, however, $T_c$ increases to above 40 K (Chen et al., 2008a,c). The highest $T_c \approx 55$ K of the Fe-based superconductors is also achieved in the Sm compound (Ren et al., 2008). The absence of the $s$-wave pair-breaking by local magnetic ions, therefore, strongly suggests an unconventional superconductivity in the Fe-based materials. The rush to the “iron age” of high-$T_c$ superconductors is henceforth unleashed (Ishida et al., 2009).

Thousands of papers have been published on Fe-based superconducting materials and comprehensive reviews already exist (Ishida et al., 2009; Johnston, 2010; Stewart, 2011). Here the scope is limited to physics picture derived mainly from our neutron scattering investigation. Personal viewpoints are expressed in order to stimulate discussion in the active and evolving field. We also limit ourselves to a sketchy outline to emphasize the main points. Original publications should be consulted for details.

II. ORBITAL ORDERING: THE COMMON MECHANISM FOR THE STRUCTURAL AND ANTIFERROMAGNETIC TRANSITIONS

Band-structure theory provides the first glimpse of electronic structure in the Fe-based superconductors...
A prominent feature is the pair of quasi-two-dimensional hole and electron Fermi surfaces that are mostly composed of d-orbitals of Fe. This is supported by ensuing ARPES measurements from various groups. The nesting of the hole and electron Fermi surfaces would naturally lead to a spin-density-wave (SDW) antiferromagnetic order (Cao et al., 2008; Dong et al., 2008; Han et al., 2008; Ma and Lu, 2008). Neutron diffraction observation of an antiferromagnetic order at the predicted in-plane wave-vector (de la Cruz et al., 2008) has been hailed as the proof of the SDW theory.

However, the same neutron diffraction work uncovers that the expected SDW gap in transport property (Han et al., 2008) occurs not at the antiferromagnetic transition, but at a separated structural transition at a higher temperature $T_S$ (de la Cruz et al., 2008). This important fact cannot be explained by the SDW theory and, unfortunately, has been ignored by most studies in the field. The SDW mechanism is a well-established way for a weak-coupling metal to acquire antiferromagnetic long-range order, such as in Cr (Fawcett, 1988; Lomer, 1962). However, experimental results of the Fe-based materials accumulated over time have indicated the necessity of supplementing it by localized spin features such as orbital ordering.

A monoclinic $P112/n$ unit cell, which is easier to compare with the ZrCuSiAs (1111) $P4/nmm$ tetragonal unit cell, was used for the distorted lattice below $T_S$ in the initial neutron diffraction work on LaFeAsO (de la Cruz et al., 2008). Since then, the consensus space group to describe the low-temperature structure has been the orthorhombic $C'mma$ (Nomura et al., 2008). The antiferromagnetic structure in the orthorhombic unit cell is determined for the first time in the neutron diffraction work on NdFeAsO (Qiu et al., 2008a). The antiferromagnetic wave-vector is $(100)$ below 2 K and the easy-axis of the Fe moment is also along the elongated $a$-axis in the basal plane. The staggered moment is $0.9(1)\mu_B$ per Fe at 0.3 K.

When the Nd moments enter the paramagnetic state above 2 K, the antiferromagnetic wave-vector of the Fe sublattice is switched to $(10\frac{1}{2})$ with a much reduced staggered moment of $0.25(7)\mu_B$ per Fe (Chen et al., 2008a), which has been overlooked in our previous work (Qiu et al., 2008a). The Nd antiferromagnetic order changes the Fe inter-layer magnetic coupling from antiferromagnetic to ferromagnetic and enhances the Fe staggered moment. However, it does not affect the in-plane Fe moment arrangement. The same in-plane Fe antiferromagnetic structure as that in NdFeAsO with both the antiferromagnetic wave-vector and moment easy-axis along the $a$-axis in basal plane (Qiu et al., 2008a) is later confirmed also for CeFeAsO (Zhao et al., 2008a), PrFeAsO (Kimber et al., 2008) and CeFeAsO (Huang et al., 2008a) with neutron diffraction. Note that the perpendicular depiction of the Fe moment and the antiferromagnetic wave-vector in Fig. 4 of Ref. (de la Cruz et al., 2008) needs to be rectified.

In BaFe$_2$As$_2$, the resistivity anomaly does concur with antiferromagnetic transition as expected by the SDW theory, however, so does the structural transition deforming from the tetragonal $I4/mmm$ ThCr$_2$Si$_2$ (122) structure (Huang et al., 2008a). As in the 1111 parent compounds, both the in-plane component of the antiferromagnetic wave-vector (101) and the Fe easy-axis are along the elongated $a$-axis of the orthorhombic $Fmmm$ unit cell. The staggered moment is $0.87(3)\mu_B$ per Fe at 5 K. Almost identical antiferromagnetic order is also found in SrFe$_2$As$_2$ (Zhao et al., 2008c) and CaFe$_2$As$_2$ (Goldman et al., 2008).

The Fe moments in both the 1111 and the 122 families of parent compounds align parallel to each other between the shortest nearest-neighbor (n.n.) pairs along the $b$-axis, and they align antiparallel between the elongated n.n. pairs along the $a$-axis. Namely, the antiferromagnetic bond shrinks and the ferromagnetic bond expands in the FeAs plane in both families. One might argue that the SDW mechanism drive the 122 system to an antiferromagnetic transition and the magnetostriction leads to the lattice distortion at the same time. However, as mentioned above, the lattice distortion predates the antiferromagnetic transition in the 1111 system. Thus it cannot be caused by magnetostriction during a magnetic transition.

Alternatively, if one assumes an orbital ordering that realizes preferred occupation of one $d$-orbital in the $a$-axis and another $d$-orbital in the $b$-axis, it could naturally lead to expanded antiferromagnetic bonds in one in-plane direction and shortened ferromagnetic bonds in the other. We have advocated the $dz^2$ and $d_y^2$ orbitals for such differentiated roles since our NdFeAsO work (Qiu et al., 2008a) together with the $ab$ initio work by one of our co-workers (Yildirim, 2008). Historically, Goodenough (Goodenough, 1955) came up with different orbital orders to form orbitally ordered lattices, which leads to the desired super-exchange or double-exchange interactions between spin pairs, to account for various magnetic orders observed in neutron diffraction work on manganites by Wollan and Koehler (Wollan and Koehler, 1955). For review on recent studies, refer to (Imada et al., 1998).

When orbital ordering occurs, a structural transition will appear, which will generally establish a new spin Hamiltonian (Bao et al., 1997a,b). When the magnetic transition temperature of the new spin Hamiltonian is lower than the orbital transition temperature, magnetic transition will occur after the structural transition upon cooling. We have investigated such a behavior in our previous neutron scattering study on manganites (Bao et al., 1997a), and the 1111 family of parent compounds belong to this type. When the magnetic transi-
tion temperature of the new spin Hamiltonian is higher than the orbital transition temperature, magnetic transition will occur in a first-order transition as soon as the structural transition occurs. We have also encountered such a behavior in our previous neutron scattering study on vanadium sesquioxides (Bao et al., 1997b), and the 122 family of parent compounds belong to this type (Huang et al., 2008a).

Also belonged to the latter type are the 11 family of parent compounds Fe$_{1+y}$(Te$_{1-x}$Se$_x$)$_2$ (Bao et al., 2009), in which magnetic and structural transitions occur simultaneously. Here, the SDW theory completely fails to explain the observed commensurate and incommensurate antiferromagnetic order, with the predicted antiferromagnetic wave-vector $45^\circ$ away from the observed ($\delta \frac{1}{2}$). The commensurate antiferromagnetic structure of $\delta = \frac{1}{2}$ occurs for $y < 0.08$ with a monoclinic $P2_1/m$ unit cell in metallic state, while the incommensurate one of $\delta < \frac{1}{2}$ occurs for $y > 0.08$ with an orthorhombic $Pmmn$ unit cell in semiconducting state. The amplitude of the staggered moment in both the commensurate and incommensurate structures is $2\mu_B$ per Fe, with an appreciable canting component in a generally rather complex magnetic structure. Nevertheless, the same relation between (anti-) ferromagnetic spin pair and (expanded) shortened bond length is observed, further supporting a unified orbital ordering scenario for all the three families of Fe-based superconductors (Bao et al., 2009).

The lattice Fourier transformation of the magnetic exchange constants with the signs described above which are prepared by the orbital ordering $J(Q)$, therefore, will peak at the observed antiferromagnetic wave-vector $Q_{\delta}^{\text{obs}}$ (Huang et al., 2008a; Qiu et al., 2008a), while the bare Lindhard function $\chi_0(Q,\omega = 0)$ always peaks at the same nesting wave-vector in the 1111, 122 and 11 parent compounds (Cao et al., 2008; Dong et al., 2008; Han et al., 2008; Ma and Lu, 2008). In the RPA approximation, the magnetic susceptibility is

$$\chi(Q,\omega) = \frac{\chi_0(Q,\omega)}{1 - J(Q)\chi_0(Q,\omega)}.$$  

Thus, one can image that in the 1111 and the 122 families, the orbital ordering and the Fermi surface work in step in realizing the observed antiferromagnetic structure, since both the $J(Q)$ and $\chi_0(Q,\omega = 0)$ peak around the nesting wave-vector. In the 11 family, however, they work out of step. The $J(Q)$ peaking at $(\delta, 0)$ dominates over the $\chi_0(Q,\omega = 0)$ and moves the peak of $\chi(Q,\omega = 0)$ from the nesting wave-vector to the observed $(\delta, 0)$.

The commensurate antiferromagnetic order in the 11 parent compounds has been investigated previously in 1975 by Fruchart et al. (Fruchart et al., 1975) and also in a later work (Li et al., 2009). The staggered moment in (Li et al., 2009) is similar to that found in our work (Bao et al., 2009). Note that the appreciable canting component observed in experiments is often neglected in popular “bi-linear” depiction of the commensurate antiferromagnetic order.

The electronic hopping, either real in determining the double-exchange or virtual in the super-exchange, should be reflected in transport (Goodenough, 1955; Imada et al., 1998). Since magnetic exchange constants in the $a$-axis and $b$-axis have different signs, in-plane anisotropy in transport properties is expected and data have begun to appear since 2010 in measurements of detwinned 122 parent compounds (Tanatar et al., 2010). The static measurement of the in-plane transport anisotropy has been extended later to frequency up to 2eV in optical spectroscopic study on detwinned BaFe$_2$As$_2$ (Nakajima et al., 2011). The preferred occupation of the $d_{xz}$ orbital at $k_z \sim \pi$ observed in polarization-dependent ARPES study on BaFe$_2$As$_2$ offers a more direct evidence for orbital ordering (Shimojima et al., 2010).

In addition to the theoretical study of Yildirim (Yildirim, 2008), there has been persistent albeit small theoretical pursuit on orbital ordering in the Fe-based superconductors (Bascones et al., 2012; Chen et al., 2010; Daghhofer et al., 2010; Lee et al., 2009; Ly et al., 2009). The recently observed block antiferromagnetic order in vacancy-ordered $A_2$Fe$_2$Se$_5$ (Bao et al., 2011; Ye et al., 2011), to be presented later, can also be understood together with those observed in the 1111 (Qiu et al., 2008a), 122 (Huang et al., 2008a) and 11 (Bao et al., 2009) compounds in a unified orbital ordering scenario (Ly et al., 2011; Yin et al., 2012).

### III. STRUCTURAL CONTROL OF SUPERCONDUCTIVITY

Superconductivity is achieved by doping the 1111 and 122 parent compounds to suppress the structural and antiferromagnetic transitions (Kamihara et al., 2008; Rotter et al., 2008a). Doping with charges of opposite sign (Lethe-Jasper et al., 2008; Sefat et al., 2008; Wen et al., 2008), isovalent substitution (Jiang et al., 2009) and high pressure or uniaxial stress (Matsubayashi et al., 2009; Torikachvili et al., 2008; Yu et al., 2009) also work. The FeSe (Hsu et al., 2008) and LiFeAs (Wang et al., 2008) do not require intentional doping, but the samples are nonstoichiometric and already in the $P4/nmm$ tetragonal PbO (11) or PbFCl (111) structure. Therefore, antiferromagnetic order seems to be a competing phase to superconductivity. Doping, chemical pressure, and physical pressure aim to suppress the structure distortion and its accompanying antiferromagnetic order.

Superconducting phase is dome-like in the tetragonal phase for the 1111 and 122 Fe-based superconductors. There have been several proposals concerning which material parameter is crucial in controlling the super-
coercivity. Lee et al. (Lee et al., 2008) and Qiu et al. (Qiu et al., 2008a) have proposed in 2008 that the closer the As-Fe-As angle is to the ideal tetrahedral angle $\arccos \left( -\frac{1}{3} \right) = 109.47^\circ$, the higher the $T_c$ is.

This local structural mechanism has survived since the initial studies on the 1111 system. It obviously links closely with the orbital ordering scenario for the antiferromagnetic order. A less perfect Fe-As tetrahedron environment would lift the $d$ orbital degeneracy and differentiate the $d$ orbitals, thus favor the antiferromagnetic instability.

IV. COEXISTENCE OF SUPERCONDUCTIVITY AND ANTIFERROMAGNETISM

While antiferromagnetic order and superconductivity look like competing order parameters, an important fine point is whether they can coexist in part of the phase diagram.

For the 1111 system, competing claims exist. On the one hand, antiferromagnetic phase and the superconducting phase are mutually exclusive, such as in the investigations on the Ce (Zhao et al., 2008a) and La systems (Huang et al., 2008) [Luetkens et al., 2009]. One the other hand, antiferromagnetic phase and the superconducting phase can coexist, such as in the studies on the La (Takeshita et al., 2008) and Sm (Drew et al., 2009) system. It is not clear whether the difference is real or is caused by the difficulty in sample synthesis control, given the narrow composition region where the difference in claims occurs.

To address the issue, we investigate the phase diagram of the K-doped BaFe$_2$As$_2$ system. The system has the merit that the whole composition range from Ba to K can be synthesized (Sasmal et al., 2008). By combining neutron diffraction, synchrotron x-ray diffraction and bulk measurements, we find that the simultaneous magnetic and structural transition of BaFe$_2$As$_2$ is suppressed by K doping. However, the superconducting phase emerges before the antiferromagnetic order is completely suppressed. We establish that the coexistence of antiferromagnetic phase and the superconducting phase is an intrinsic property of the system (Chen et al., 2009).

There are other views. The first is that the structural and antiferromagnetic transitions are separated ones. We found in the case of BaFe$_2$As$_2$ that the separation is likely caused by flux-contaminated single-crystal samples used (Kofu et al., 2009). Our conclusion of the simultaneous magnetostructural transition has been confirmed by a recent diffraction work using high quality (Ba,K)Fe$_2$As$_2$ samples (Avci et al., 2011).

The second claim is that the samples phase-separate into an antiferromagnetic phase and a superconducting phase, instead of coexisting as shown in our study. It is understandable that one fails to make homogeneous samples when a new material first appears before the correct recipe is widely known. However, these two claims due to poor sample quality have been so widely propagated that they have permeated many otherwise respectable reviews and perspective pieces, e.g. in (Mazin, 2010). The coexistence of antiferromagnetism and superconductivity in (Ba,K)Fe$_2$As$_2$ has been corroborated using a different experimental technique in recent NMR studies (Li et al., 2012; Urbano et al., 2010).

We used nominal sample composition in our study (Chen et al., 2009). Rotter et al. did a better job in determining the sample composition in a slightly later study (Rotter et al., 2009b). However, they did not investigate the antiferromagnetic phase transition and the coexistence problem. Avci et al. refine the sample compositions in their systematic work (Avci et al, 2011).

Since our study on the hole-doped phase-diagram using the (Ba,K)Fe$_2$As$_2$ system as the prototype, phase-diagrams of electron-doping using Co or other transition metal elements at the Fe site, and isovalent substitution of As by P (Jiang et al., 2009) have also been established to show the coexistence as a general feature in the 122 system. Pressure phase-diagram has also been obtained but it is extremely sensitive to the hydrostatic condition (Matsubayashi et al., 2009; Yu et al., 2009), not completely surprising for their two-dimensional crystalline structures.

Theoretical consequences of the coexistence have been reviewed recently (Hirschfeld et al., 2011).

V. WEAK LOCALIZATION AND SUPERCONDUCTIVITY

The discovery of the 11 superconductors expands the scope of Fe-based high-$T_c$ superconductors from pnictides to less poisonous chalcogenides (Hsu et al., 2008). The original 11 superconductor contains more iron than selenium, and it was initially considered to form in the PbO structure with Se deficiency. We refine the isostructural iron telluride and find that it forms in the PbFCl (111) structure of the same space group with the excess Fe(2) occupying the same site as the Li in LiFeAs (Bao et al., 2009). This is also the case found later for iron selenide (McQueen et al., 2009). Thus the customary classification of 11 and 111 families of Fe-based superconductors is less structural than electronic in balancing the Se$^{-2}$ and As$^{-3}$ ions respectively.

The isovalent substitution of Se by Te has not affected $T_c \approx 8$ K much until a first-order jump to the $T_c \approx 14$ K phase (Fang et al., 2008; Yeh et al., 2008). Close to the Te end of the phase diagram, there exists an antiferromagnetic phase in a narrow composition range (Liu et al., 2010). The magnetic structure, crystal symmetry, and transport property are different in the two phases at the Te end tuned by the amount of the excess Fe (Bao et al., 2009), which has been presented above. What we con-
cern here is the strong spin-glass low-energy magnetic fluctuations left in the samples after the long-range antiferromagnetic order is suppressed by Se substitution of Te.

It turns out that four n.n. spins on the Fe square lattice in the tetragonal P4/nmm phase tend to form a super-spin block, and these block spins then form a chessboard antiferromagnetic pattern. However, this tendency somehow cannot develop into a long-range order, and a short-range order is instead nucleated by the excess Fe and becomes spin-glass at low temperature (Thampy et al., 2012). On the other hand, magnetic entropy is released near the Te end through the usual route of structural transition for frustrated magnetic systems: The new spin Hamiltonian prepared by the orbital ordering allows magnetic transition at higher temperature.

We have shown that the more the excess Fe is, the stronger the low-energy short-range antiferromagnetic fluctuations are. When the magnetic fluctuations are strong enough, their scattering turns metallic resistivity to logarithmic divergence (Liu et al., 2010). Bulk superconductivity in Fe(Te,Se) occurs only when normal state transport is metallic. Therefore, when low-energy scattering leads to weak localization to break the Fermi liquid phase coherence of the Bloch wave function, superconductivity is destroyed.

As will be presented, a variation of this behavior happens in the Fe-vacancy ordered iron chalcogenide superconductors.

VI. STRUCTURAL AND MAGNETIC EXCITATIONS

Electron-phonon interaction plays a central role in the BCS theory of superconductivity. When triple-axis inelastic neutron scattering spectrometer was invented, its major application was to measure the spectrum of phonon. Theoretical and experimental studies together have propelled ab initio calculation of phonon spectrum to a very high reliability for most materials. When the discovery of the 1111 Fe-based high Tc superconductivity was reported, theoretical phonon spectrum was used to calculate Tc and it was concluded that phonon are not energetic enough to support the high value of Tc (Boeri et al., 2008).

To check the reliability of the conclusion, we try to verify the energy scale of the theoretic phonon spectrum in the La-1111 superconductor (Tc = 26 K) (Qiu et al., 2008). This can be readily performed by comparing the peak energy due to van Hove singularity in phonon density of states with the theoretic value, and the theory is indeed found to be reliable. The check was repeated with coarser energy resolution to cover the whole phonon band and the same conclusion is reached (Christianson et al., 2008). Studies on phonon density of states for BaFe2As2 (Mittal et al., 2008) and FeSe (Phelan et al., 2009) have also been performed.

Meanwhile, theories for the magnetic origin of the high-Tc superconductivity in iron pnictides are advanced. Similar to the case for cuprate superconductors, d-wave was a popular choice. Thus, it was a big surprise that an isotropic superconducting gap was announced in an Andreev reflection study on SmFeAsO0.85F0.15 (Chen et al., 2008). The nodeless superconducting gaps are demonstrated shortly by ARPES measurement of Ba0.6K0.4Fe2As2 (Ding et al., 2008). The focus then shifts to the s± symmetry for the Cooper pairs (Mazin et al., 2008).

ARPES cannot detect the sign change from the electron to hole Fermi surface. However, the sign change will lead to a “resonance peak” which can be measured by inelastic neutron scattering (Korshunov and Eremin, 2008; Maier et al., 2009). We try but fail to detect such a resonance peak in an optimally doped LaFeAsO0.87F0.13 polycrystalline sample (Qiu et al., 2008), possibly because the superconducting volume fraction is too small. The first successful observation of the resonance peak is from a polycrystalline sample of Ba0.6K0.4Fe2As2 (Christianson et al., 2008). When large single crystal samples of the 122 system become available, the spatial distribution of the resonance peak can be investigated and its two-dimensionality is convincingly demonstrated (Lumsden et al., 2009).

After the discovery of the 11 superconductors, large single crystals of the 14 K Fe(Te,Se) superconductors are soon available. In addition to the expected resonance peak, it is shown that the magnetic excitations are fully gapped in the superconducting state (Qiu et al., 2009). While the intensity of the resonance peak decreases with the rising temperature in the BCS fashion, the peak energy itself is observed to be temperature independent. The spectral weight of the resonance peak comes from gapping the inclined normal state spin excitation continuum originating from a pair of perpendicular incommensurate points (Argyriou et al., 2010). Here, the normal state magnetic excitation spectrum is entirely of a typical itinerant antiferromagnet to which spin-wave theory is not applicable (Bao et al., 1996). No “hour-glass” type of excitations are present in our data and we suspect that it is due to superposition of signals from superconducting and non-superconducting portions contained in inhomogeneous samples.

There have been reports of resonance peak observed in other polycrystalline 1111 superconductors. However, the signal to noise ratio seems too low to be conclusive at this time. More recently, quality single crystals of the NaFeAs superconductor are successfully grown. Dai et al. have observed beautiful resonance peak from the samples to be published.

The search for superconducting resonance peak in Fe-based superconductors has been inspired by the theory for the s± symmetry (Korshunov and Eremin, 2008).
Maier et al. (2009) and Mazin et al. (2008) and it has fulfilled the theoretical expectation. However, it has been recently pointed out that the \( s^\pm \) pairing function is not a parity eigenstate when the full local symmetry of the FeAs or FeSe layer is considered. The neutron resonance data would support an odd parity state over the even parity state in the new theoretical scheme (Hu et al. 2013). Different from neutron scattering investigation on magnetic excitations in Fe-based superconductor, such investigation in cuprate superconductors proceeded from parent compounds to superconducting compounds. First of all, quality samples suitable for inelastic neutron scattering study became available initially only for the parent cuprates. Secondly, magnetic excitations from parent insulating antiferromagnet are spin-waves and they are theoretically easy to be analyzed. For iron pnictides, even the parent compounds are metallic and itinerant antiferromagnetic excitations are important. Even so, at least the lower energy parts of the magnetic excitations have been reported to be spin-waves for some parent compounds and they are readily analyzable (Diallo et al. 2009). A recent review of experimental and theoretical results can be found in Ref. (Dai et al. 2012). However, as mentioned above, for the 11 superconductors, spin-wave theory completely fails (Argyriou et al. 2010).

VII. THE 245 SUPERCONDUCTORS

In 2010, a 30 K superconductor of the nominal composition \( \text{K}_0.8\text{Fe}_2\text{Se}_2 \) is reported (Guo et al. 2010). The chemical formulas indicates a deep electronic doping and ARPES data are consistent with such an electron counting (Zhang et al. 2011). However, the single crystal samples grown with the same method by the same group as those used in the ARPES experiment are shown by x-ray single crystal diffraction to be \( \text{K}_0.775(4)\text{Fe}_{1.613(1)}\text{Se}_2 \) and \( \text{Cs}_0.748(2)\text{Fe}_{1.626(1)}\text{Se}_2 \) (Zavalij et al. 2011). Another superconducting single crystal supplied by the second group is refined to be \( \text{K}_0.737(6)\text{Fe}_{1.631(3)}\text{Se}_2 \). The superconducting sample of slightly different nominal composition from the second group was used in neutron powder diffraction study, and the sample composition is refined to be \( \text{K}_0.831(2)\text{Fe}_{1.641(3)}\text{Se}_2 \) (Bao et al. 2011).

While we cannot determine whether K or Cr is ordered in the crystal, Fe vacancies form an almost perfect \( \sqrt{5} \times \sqrt{5} \) superlattice in the superconducting samples (Bao et al. 2011). The refined chemical formulas is close to \( \text{K}_0.8\text{Fe}_{1.6}\text{Se}_2 \). It can be rewritten as \( \text{A}_2\text{Fe}_3\text{Se}_2 \). Thus, we call the new family of superconducting single crystal diffraction to be \( \text{K}_0.8\text{Fe}_{1.6}\text{Se}_2 \). The neutron resonance measurement temperature of 100 and 90 K respectively, the two samples also show the \( \sqrt{5} \times \sqrt{5} \) superlattice order. However, the departure from the ideal \( \text{K}_0.8\text{Fe}_{1.5}\text{Se}_2 \) formulas necessitates the partial filling of the “vacant” Fe2 site and a deficiency in the “full” Fe1 site.

Such an imperfect \( \sqrt{5} \times \sqrt{5} \) Fe vacancy order exists in an intermediate temperature range even in non-superconducting sample \( \text{K}_0.99\text{Fe}_{1.48}\text{Se}_2 \) (Bao et al. 2013). Close to be \( \text{KF}_{1.5}\text{Se}_2 \), namely one vacancy out of four Fe sites, the perfect \( 2\sqrt{2} \times 2\sqrt{2} \) pattern occurs only in part of the sample in the temperature window of from 295 to 500 K. This can be understood in the two-level statistical physics model provided that the \( \sqrt{5} \times \sqrt{5} \) lattice structure is lower than the \( 2\sqrt{2} \times 2\sqrt{2} \) structure in energy. In calculating these energies, the observed block antiferromagnetic order and its associated lattice tetramerization (Bao et al. 2011) should be included in the equation (Hao and Dai 2011; Yan et al. 2011).

All these samples can be written as \( \text{K}_x\text{Fe}_{2-y}\text{Se}_2 \) with \( x \sim 2y \). Namely, with \( \text{K}^{+1} \) and \( \text{Se}^{-2} \), valence of Fe \( \sim 2 \) (Bacsca et al. 2011; Bao et al. 2011, 2013; Zavalij et al. 2011). The phase-diagram is provided in (Bao et al. 2013). Note that the order-disorder structural transitions occur at \( T_N \) and \( T^* \), and it is remarkable that Fe ions remain mobile at such low temperatures. It is useful to keep these information in mind if one want to image the element movement during the sample annealing process.

Among the discoverers of the 245 superconductors, Fang et al. distinguishes themselves in intentionally introducing Fe vacancy into the Fe square lattice, as reflected in the original arXiv article title (Fang et al. 2011; Wang et al. 2011). The \( T^* \) approaches zero in the \( (\text{Tl},\text{K})\text{Fe}_x\text{Se}_2 \) system (Fang et al. 2011) which resembles the usual magnetic susceptibility behavior at \( T_N \) (Bao et al. 2013), but the anomaly in magnetic susceptibility is caused by the large magnetic excitation gap due to the moment-space anisotropy in the \( \sqrt{5} \times \sqrt{5} \) phase (Chi et al. 2013). For all the five members of the 245 superconductors, \( T_N \) stays high above room temperature, ranging from 471 to 559 K (Ye et al. 2011). The strong interaction between the antiferromagnetic and superconducting orders is reflected in the anomaly in magnetic order parameter near \( T_c \). The imperfect \( \sqrt{5} \times \sqrt{5} \) vacancy order will contribute to impurity scattering to conducting electrons. Resistivity traces the degree of the order well, changing from semiconducting to logarithmic divergence and then to metallic when the sample composition approaches the ideal 245 formulas (Bao et al. 2013). Like in the 11 superconductors, superconductivity occurs when the normal state transport is metallic with minimum scattering from imperfect vacancy order.

Different from all previous antiferromagnetic orders found in the Fe-based superconductor systems, antiferromagnetic order in the 245 superconductors does not break the four-fold symmetry of the \( \text{I}_4/m \) lattice struc-
ture [Bao et al., 2011]. Differentiation of magnetic exchange interactions therefore is not in the a-axis or b-axis direction but in the intra or inter-four-spin blocks. Magnetic excitations of the \((\text{Ti,} \text{Rh})_2\text{Fe}_4\text{Se}_5\) superconductor have been measured recently and the spin-wave theory including the n.n. and n.n.n. intra and inter-block exchange constants well describes the data [Chi et al., 2013]. The success of the spin-wave theory is not surprising given that the staggered moment \(3.3\mu_B\) per Fe is very close to the atomic limit value \(4\mu_B\).

With the volatile alkali element and highly mobile Fe, the \(A_2\text{Fe}_2-y\text{Se}_y\) crystal often contains plate-like intergrowth of Fe [Bao et al., 2011]. Thus, extra Fe is included in the nominal sample composition determined by inductively coupled plasma analysis. Another common error is identifying the 245 phase with \(A_2\text{Fe}_2\text{Se}_5\) and we have provided the non-superconducting refinement examples \(K_0.99\text{Fe}_4\text{Se}_5\) [Krajewski et al., 2006], \(K_0.93\text{Fe}_4\text{Se}_5\), and \(K_0.86\text{Fe}_1.56\text{Se}_2\) above [Bacs et al., 2011]. Many samples in the \(14/m\) insulator phase of the phase-diagram shown in Fig. 4 of Ref. [Bao et al., 2013] have been misidentified as \(A_2\text{Fe}_4\text{Se}_5\) in the current literature.

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REFERENCES

Argyriou, D. N., A. Hiess, A. Akbari, I. Eremin, M. M. Korshunov, J. Hu, B. Qian, Z. Mao, Y. Qiu, C. Broholm, and W. Bao (2010), Phys. Rev. B 81, 220503(R).

Avci, S., O. Chmaissem, E. A. Goremychkin, S. Rosenkranz, J.-P. Castellan, D. Y. Chung, I. S. Todorov, J. A. Schlueter, H. Claus, M. G. Kanatzidis, A. Daoud-Aladine, D. Khalyavin, and R. Osborn (2011), Phys. Rev. B 83, 172503.

Bacs, J., A. Ganin, Y. Takabayashi, K. Christensen, K. Prasides, M. Rosseinsky, and J. Claridge (2011), Chem. Sci. 2, 1054.

Bao, W., C. Broholm, J. M. Honig, P. Metcalf, and S. F. Trevino (1996), Phys. Rev. B 54, R3726.
Qiu, Y., W. Bao, Y. Zhao, C. Broholm, V. Stanev, Z. Tesanovic, Y. C. Gasparovic, S. Chang, J. Hu, B. Qian, M. Fang, and Z. Mao (2009), Phys. Rev. Lett. 103, 067008.
Ren, Z. A., W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao (2008), Chin. Phys. Lett. 25, 2215.
Rotter, M., M. Pangerl, M. Tegel, and D. Johrendt (2008a), Angew. Chem. Int. Ed. 47, 7949.
Rotter, M., M. Tegel, and D. Johrendt (2008b), Phys. Rev. Lett. 101, 107006.
Sasmal, K., B. Lv, B. Lorenz, A. Guloy, F. Chen, Y. Xue, and C. W. Chu (2008), Phys. Rev. Lett. 101, 107007.
Sefat, A. S., R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus (2008), Phys. Rev. Lett. 101, 117004.
Shimojima, T., K. Ishizaka, Y. Ishida, N. Katayama, K. Ohgushi, T. Kiss, M. Okawa, T. Togashi, X. Y. Wang, C.-T. Chen, S. Watanabe, R. Kadota, T. Oguchi, A. Chainani, and S. Shin (2010), Phys. Rev. Lett. 104, 057002.
Siegrist, T., H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. P. Jr (1994), Nature 367, 254.
Singh, D. J., and M.-H. Du (2011), Phys. Rev. Lett. 100, 237003.
Stewart, G. R. (2011), Rev. Mod. Phys. 83, 1589.
Takeshita, S., R. Kadono, M. Hiraishi, M. Miyazaki, A. Koda, Y. Kamihara, and H. Hosono (2008), J. Phys. Soc. Jpn. 77, 10370.
Tanatar, M., E. Blomberg, A. Kreysig, M. Kim, N. Ni, A. Thaler, S. Bud’ko, P. Canfield, A. Goldman, I. Mazin, and R. Prozorov (2010), Phys. Rev. B 81, 184508.
Thampy, V., J. Kang, J. A. Rodriguez-Rivera, W. Bao, A. T. Savici, J. Hu, T. J. Liu, B. Qian, D. Fobes, Z. Q. Mao, C. B. Fu, W. C. Chen, Q. Ye, R. W. Erwin, T. R. Gentile, Z. Tesanovic, and C. Broholm (2012), Phys. Rev. Lett. 108, 107002.
Torikachvili, M., S. Bud’ko, N. Ni, and P. Canfield (2008), Phys. Rev. Lett. 101, 057006.
Urbano, R. R., E. L. Green, W. G. Moulton, A. P. Reyes, P. L. Kuhns, E. M. Bittar, C. Adriano, T. M. Garitezi, L. Bufaical, and P. G. Pagliuso (2010), Phys. Rev. Lett. 105, 107001.
Wang, H., C. Dong, Z. Li, S. Zhu, Q. Mao, C. Feng, H. Q. Yuan, and M. Fang (2011), Europhys. Lett. 93, 47004.