Enhanced low-energy magnetic excitations evidencing the Cu-induced localization in an Fe-based superconductor Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$

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We have performed inelastic neutron scattering measurements on optimally-doped Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ and 10% Cu-doped Fe$_{0.88}$Cu$_{0.12}$Te$_{0.5}$Se$_{0.5}$, to investigate the substitution effects on the spin excitations in the whole energy range up to 300 meV. It is found that substitution of Cu for Fe enhances the low-energy spin excitations ($\leq 100$ meV), especially around the (0.5, 0.5) point, and leaves the high-energy magnetic excitations intact. In contrast to the expectation that Cu with spin 1/2 will dilute the magnetic moments contributed by Fe with a larger spin, we find that the 10% Cu doping enlarges the effective fluctuating moment from 2.85 to 3.13 $\mu_B$/Fe, although there is no long- or short-range magnetic order around (0.5, 0.5) and (0.5, 0). The presence of enhanced magnetic excitations in the 10% Cu doped sample which is in the insulating state indicates that the magnetic excitations must have some contributions from the local moments, reflecting the dual nature of the magnetism in iron-based superconductors. We attribute the substitution effects to the localization of the itinerant electrons induced by Cu dopants. These results also indicate that the Cu doping does not act as electron donor as in a rigid-band shift model, but more as scattering centers that localize the system.

I. INTRODUCTION

In both copper- and iron-based high-temperature superconductors, understanding the interplay between superconductivity and magnetism has been a central issue.$^{[1-7]}$ In this regard, doping has acted as an extremely powerful tuning parameter. For example, for iron pnictides, rich phase diagrams have been obtained by substituting Fe with 3d transition metals (TMs). With the isovalent doping of TM (TM=Co, Ni), the antiferromagnetic order in the parent compound is suppressed, and superconductivity appears with the superconducting temperature ($T_c$) vs. doping having a dome shape.$^{[8,9]}$ In the superconducting phase, a resonance peak in the paramagnetic excitations with the energy below twice of the superconducting gap is typically observed$^{[10,13]}$. An initial picture to understand the doping effect was the rigid-band model, which considered the extra $d$ electrons in the dopants contributing to the conduction bands$^{[14,15]}$, and resulted in a rigid-band shift of the Fermi level.$^{[16,17]}$ However, such a description has faced challenges from both theory$^{[18,19]}$ and experiment$^{[20,21]}$, as it ignores the impurity scattering induced by the dopants. For example, although Cu is next to Ni and Co, its doping effect is rather distinct from that of Co and Ni. With increasing Cu concentration, samples can be driven into an insulating phase accompanied by the development of spin glass and long-range magnetic order.$^{[22,23]}$Remarkably, in a scanning tunneling microscopy study on NaFe$_{1-x}$Cu$_x$As, it is found that the local electronic structure of the insulating sample are strikingly similar to the Mott insulating phase of a lightly doped cuprate.$^{[24,25]}$

In another widely investigated iron-based superconductor system iron chalcogenide Fe$_{1+y}$Te$_x$, where superconductivity can be induced by substituting Te with Se (Refs. 31 and 32), similar Cu substitution effects have been found. At both ends of the phase diagram of the Fe$_{1+y}$Te$_{1-x}$Se$_x$ system, the increasing doping of Cu will gradually drive Fe$_{1+y}$Te$_{1-x}$Se$_x$ to an insulating phase, as well as induce a spin-glass state. Different substitution effects of Cu and Co/Ni on optimally-doped superconducting Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ were also observed.$^{[32]}$ Comparing with the impacts of Co or Ni substitution, the suppression of superconductivity and conductivity of Cu doping is more significant. Furthermore, with 10% Cu doping, the resistivity shows a Mott-insulator behavior, which has been attributed to the stronger impurity potentials of Cu (Ref. 33). Cu doping also enhances the low-energy ($\leq 12$ meV) spin excitations significantly, but without inducing a static magnetic order, either in the long-range or short-range form.$^{[34,35]}$ However, since these measurements were only performed at low energies, it is not clear that the spectral weight
enhancement at low energies reflects the total enhancement or just a redistribution from high energies. In the former case, it means that the total fluctuating magnetic moment increases. While in the latter case, the fluctuating magnetic moments only slow down, and the total moment may remain unchanged or even decreased, consistent with the expectation for the diluting effect of Cu with a smaller spin. Therefore, inelastic neutron scattering (INS) measurements over the entire energy range will be required to make a definite conclusion.

In this paper, we investigate the effects of copper substitution on the spin excitations by performing comparative INS measurements on 10% Cu doped Fe$_{0.88}$Cu$_{0.1}$Te$_{0.5}$Se$_{0.5}$ (labeled as Cu10) and copper-free Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ (labeled as Cu0). With the large energy and momentum coverage of the time-of-flight spectrometers, we are able to uncover the full magnetic excitation spectrum. To analyze the data quantitatively, we have performed cross normalization of the data and obtained absolute values for the scattering intensities. From the normalized data, we find that the excitation up to ~100 meV has been enhanced in Cu10, while the high-energy spectrum shows negligible difference. This gives rise to an effective moment of 3.13 $\mu_B$/Fe in Cu10 than that of 2.85 $\mu_B$/Fe in Cu0. Since Cu10 is insulating, the magnetic excitations must have contributions from local moments. On the other hand, the itinerant electrons are believed to give rise to incommensurate excitations including the magnetic resonance feature around (0.5, 0.5) in Cu0 (Refs. 39–43). These results indicate the dual nature of the magnetic excitations and support that the Cu doping induces localization of the itinerant electrons and enhances the magnetic correlations.

II. EXPERIMENTAL DETAILS

Single-crystal samples of Fe$_{0.88}$Cu$_{0.1}$Te$_{0.5}$Se$_{0.5}$ and Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ (labeled as Cu10 and Cu0) were grown by the horizontal Bridgman method, as mentioned in our previous work. Each single crystal has a shape of semicylinder with two flat cleavage surfaces and a mass about 10 g. From resistivity measurement results, the Cu0 sample shows a $T_c$ of 15 K, while the Cu10 sample is an insulator and the resistivity-temperature curve can be fitted well with a three-dimensional Mott variable range hopping formula.

The INS experiments were performed on the time-of-flight spectrometers ARCS and HYSPEC, both located at SNS of Oak Ridge National Laboratory. On ARCS, multiple incident energies of $E_i$ = 60, 180, 400 meV were used with corresponding chopper frequency of 420, 600, and 420 Hz, respectively. The energy resolution for each $E_i$ is about 5% at $E = 0$ meV. Since the wave vector $Q$ and energy $E$ are coupled with fixed incident neutron momentum and sample orientation in the time-of-flight experiments, to cover a large range in the $(Q, E)$ space, the samples were rotated about the [010] axis by 90° with a step of 5° on ARCS. For the Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ sample, extra data with a step of 1° for $E_i$ = 60 and 180 meV were also collected. Data were further folded and averaged along the [100] axis to reduce noise and instrument-induced streaks by DAVE software. On HYSPEC, an incident energy of $E_i$ = 35 meV and a Fermi chopper frequency of 240 Hz was used with the energy resolution $\Delta E \approx 3$ meV at $E = 0$ meV. Both samples were rotated in the a-b plane by 90° with a step of 1° on HYSPEC. The data obtained on HYSPEC covered approximately one quadrant of the $(H, K, 0)$ plane and had been symmetrized to be four-fold to be compared with the higher-energy data collected on ARCS. On both spectrometers, the crystals were mounted on aluminum sample holders and loaded into a closed-cycle refrigerator. All neutron scattering measurements were performed at 100 K, which was well above the $T_c$ of Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ to avoid any effects from the superconducting correlations. When presenting the INS data in the reciprocal space, we used the configuration of two-Fe unit cell, of which the lattice constants at room temperature were $a = b \approx 3.8$ Å and $c = 6.1$ Å for both samples. The wave vector $Q$ was expressed as $(H, K, L)$ reciprocal lattice unit (rlu) of $(a^*, b^*, c^*) = (2\pi/a, 2\pi/b, 2\pi/c)$.

As the magnetic excitations in Fe$_{1+y}$Te$_{1-x}$Se$_x$ are reported to be of two-dimensional nature because of the much weaker interplanar correlation, we had projected the spin excitations onto the $(H, K, 0)$ plane and had been symmetrized to be four-fold to be compared with the higher-energy data collected on ARCS. On both spectrometers, the crystals were mounted on aluminum sample holders and loaded into a closed-cycle refrigerator. All neutron scattering measurements were performed at 100 K, which was well above the $T_c$ of Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ to avoid any effects from the superconducting correlations. When presenting the INS data in the reciprocal space, we used the configuration of two-Fe unit cell, of which the lattice constants at room temperature were $a = b \approx 3.8$ Å and $c = 6.1$ Å for both samples. The wave vector $Q$ was expressed as $(H, K, L)$ reciprocal lattice unit (rlu) of $(a^*, b^*, c^*) = (2\pi/a, 2\pi/b, 2\pi/c)$.

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TABLE I. Parameters of normalization for Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$ (Cu0) and Fe$_{0.88}$Cu$_{0.1}$Te$_{0.5}$Se$_{0.5}$ (Cu10) with the phonon data obtained on the HYSPEC spectrometer.

| Sample | $Q$ (rlu)       | $E$ (meV) | $n_q$ ($T = 100$ K) | $\frac{k_B^2}{2m}$ (meV) | $\int \tilde{I}(Q, E)dE$ (meV$^{-1}$) | $|F_N(G)|^2$ (b) | $\frac{1}{N_{R0}}$ (meV$^{-1}$ b) |
|--------|----------------|-----------|---------------------|--------------------------|-------------------------------------|----------------|----------------------------------|
| Cu0    | (0,-2.140,0)   | 5.000     | 2.258               | 25.94                    | 0.0051                              | 11.29          | 81.49                            |
|        | (0,-1.830,0)   | 4.928     | 2.280               | 18.97                    | 0.0047                              | 11.29          | 66.12                            |
| Cu10   | (0,-2.140,0)   | 5.065     | 2.230               | 25.94                    | 0.0041                              | 11.00          | 95.34                            |
|        | (0,-1.860,0)   | 4.410     | 2.480               | 19.60                    | 0.0041                              | 11.00          | 91.51                            |

FIG. 1. Constant-energy contour maps and line cuts of the magnetic excitations at 100 K for Fe$_{0.88}$Cu$_{0.1}$Te$_{0.5}$Se$_{0.5}$ and Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$. Panels (a-f) and (g-l) present constant-energy contours for Cu10 and Cu0 samples, respectively. The measurements in (a) and (g) were carried out on HYSPEC and the data were symmetrized to be four-fold symmetric, while the data on ARCS in the other panels were folded along the $H$ axis to the $K \geq 0$ side and then the folded data were duplicated on the $K \leq 0$ side to represent the four-fold symmetry. The streaks across the excitations in panels (g) and (h) to (j) were due to the lack of detector coverage wherein. Panels (m-r) are linear cuts of the spin excitations through (-0.5, 0.5) along the [110] direction, illustrated as the dashed line in panel (a), at the corresponding energies labeled in the same column. The errors through data points represent one standard deviation throughout the paper. Solid lines through data are fitted with Gaussian functions. The data integration range for the linear cuts are $H = K = \pm 0.025$ rlu.

Here $q = Q - G$ is the reduced wave vector, and $n_q = 1/(1 - e^{-E/k_B T})$ is the Bose factor. $m$, $M$, $F_N(G)$, and $\beta$ are the neutron mass, atomic mass of one unit cell, the acoustic phonon structure factor at Bragg peak $G$ near $Q$ at which the acoustic phonon is measured, and the angle between $Q$ and phonon polarization direction. By performing constant-$Q$ scans, one can fit the scans and obtain the final integrated phonon intensity $\int \tilde{I}(Q, E)dE$. To improve the reliability of our data, we chose the data from HYSPEC with better energy resolution as the reference points for cross-normalization. The data on ARCS had also been normalized with phonons measured with $E_i = 60$ meV and then cross checked with the HYSPEC data where they had overlapping energy ranges. The determined parameters for the normalization of the HYSPEC data are presented in TABLE I. Averaged values of the resolution volume $N_{R0}$ at different $Q$s were taken when calculating $S(Q, E)$.

### III. RESULTS AND ANALYSES

#### A. Spin excitations

To understand how the spin excitations of Cu10 sample evolve with energy, we begin with a series of constant-energy cuts of the magnetic spectra as shown in Fig. 1(a)-(f) with energy transfers up to 160 meV. Results for the Cu0 sample are arranged in the second row as Fig. 1(g)-(l), which are found to be consistent with previous measurements on a sample with similar composition FeTe$_{0.51}$Se$_{0.49}$, after considering the effect of magnetic form factor at large $Q$s (Ref. [44]). The linear-cut comparisons of Cu10 and Cu0 through (0.5, 0.5) along the [110] direction are presented in the third row as Fig. 1(m)-(r). From the energy slices of both samples, we can find differences in the peak intensities and pattern shapes at energies below $\sim65$ meV. At higher energies, the scat-
The fittings with Gaussian functions to the constant-$E$ top of the contour maps are the peak positions extracted from side folded and averaged for both panels. The data points on one side of $(-0.5, 0.5)$ has been presented, with the other direction is 0.056 rlu. For each sample, only the dispersion appears to be quite similar. Specifically, taking the second-quadrant data as representatives, two widely studied incommensurate peaks located at $(-0.5 \pm \delta, 0.5 \pm \delta)$ elongating along the $[110]$ direction can be recognized for both Cu10 and Cu0 samples, respectively. The integration range along the $[110]$ direction is 0.056 rlu. For each sample, only the dispersion on one side of $(-0.5, 0.5)$ has been presented, with the other side folded and averaged for both panels. The data points on top of the contour maps are the peak positions extracted from the fittings with Gaussian functions to the constant-$E$ scans such as those shown in Fig. 1(m)-(r). The vertical errorbars stand for the energy binning ranges used for making the fittings, and the horizontal bars are the fitting errors. Solid and dashed lines through data are guides to the eye, illustrating the dispersions for Cu10 and Cu0, respectively.

To further characterize the dispersion, we have obtained a series of such $Q$ scans from 6 to 190 meV, and plot the dispersions along the $[110]$ direction for both samples in Fig. 2. At each energy, we performed the same fitting as the lines shown in Figs. 1(m)-(r) and obtained the peak positions. As the two branches of the dispersions with positive and negative $\delta$ may not be equivalent, we have averaged $|\delta|$ for each sample in the figure. A notable separation between the dispersions of Cu10 and Cu0, with the peaks of Cu10 being closer to $(0.5, 0.5)$, is obvious below $\sim$100 meV. Above 100 meV, the dispersions for the two samples merge together. Above 160 meV, the excitations persist at around $(1, 0)$ and $(0, 1)$ without further dispersing outwards. The overall features are similar to those of FeTe$_{0.51}$Se$_{0.49}$ (Ref. 11), and remarkably, the high-energy stripe-like excitations are similar to those in the parent compound Fe$_{1+y}$Te (Refs. 18 and 17). However, before the incommensurate peaks gradually disperse to $(1, 0)$ and $(0, 1)$ at high energies, a kink occurs at about 40 meV for Cu10 and 30 meV for Cu0. Below the kink energy, the incommensurate peaks are almost dispersionless, and above it, the excitations become dispersive. We suspect the kink energy to be the characteristic energy scale that distinguishes two types of excitations—the paramagnetic excitations around $(0.5, 0.5)$ at low energies and the remnant of the spin waves in the parent compound Fe$_{1+y}$Te at high energies. Compared with the dispersion of the Cu0 sample, the dispersion Cu10 is steeper at low energies, and the kink energy is also higher. This indicates that the $(\pi, \pi)$-type spin correlation in the Cu10 sample is more robust, consistent with the spectral weight enhancement around $(-0.5, 0.5)$ as discussed above.

### B. Magnetic moments

To further investigate the evolution of the magnetic excitations with doping, we have calculated the wave-vector-integrated correlation function $S(E)$ by integrat-
can also calculate the fluctuating instantaneous effective low-energy excitation (below high-energy spectrum remains unchanged while only the electron-doped BaFe$_{2}$As$_{2}$ samples. Such phenomenon is similar to the case in the compound Fe$_{2}$As$_{2}$ (Refs. 49 and 50), where the high-energy spectrum is similar to that of the parent compound Fe$_{2}$As$_{2}$ from Refs. 17 and 48 but larger than the ~1.1 $\mu_{B}/$Fe for FeSe (Ref. 51) at 110 K. The effective local spin $S$ is 1.14 ± 0.02 for Cu10 and 1.01 ± 0.02 for Cu0, which is close to an $S = 1$ ground state with the existence of itinerant electrons at 100 K.



FIG. 3. Energy dependence of the $Q$-integrated dynamical spin-spin correlation function $S(E)$ for Fe$_{0.88}$Cu$_{0.15}$Te$_{0.5}$Se$_{0.5}$ and Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$. Integration of $S(E)$ covers an area of one Brillouin zone (-1≤H≤0, 0≤K≤1). The normalized data from different spectrometers and incident energies are consistent with each other in the overlapping regimes, indicating the reliability of the normalizations. Horizontal errorbar stand for the energy binning range, and vertical error represents one standard deviation. Solid lines through data are guides to eye. The dashed line is plotted by subtracting intensities of Cu0 from Cu10, indicating the extra intensities induced by the Cu substitution.

From our comprehensive magnetic excitation spectra in the whole energy scale on both Cu10 and Cu0 samples, we have found that while the high-energy magnetic excitations, which are likely to be the remnant of the spin waves from the parent compound, remain intact, the low-energy excitations (< 100 meV) are substantially enhanced. In addition to the intensity enhancement at the incommensurate peaks in the Cu10 sample at low energies, there is more spectral weight filling in around the commensurate position (0.5, 0.5). The velocity of the low-energy excitations and the kink energy where the low-energy excitations become dispersive are both larger in the Cu10 sample, indicating the strengthened magnetic interactions. As a result, the effective magnetic moment increases from 2.85 ± 0.06 $\mu_{B}$/Fe in Cu0 to 3.13 ± 0.06 $\mu_{B}$/Fe in Cu10, corresponding to an effective spin of 1.01 ± 0.02 and 1.14 ± 0.02 for Cu0 and Cu10, respectively. These results are in contrast to the expectation that the Cu doping will dilute the magnetic moment. Instead, it is indicated that the Cu doping will enhance the magnetic correlations around (0.5, 0.5). This resolves the uncertainties of the low-energy data in our previous works.

We believe the enhancement of the low-energy magnetic excitations around (0.5, 0.5) is at the expense of the itinerancy of the Fe electrons. In our previous works, we have shown from the resistivity measurements that the Cu doping will suppress the itinerancy of the system dramatically—with a 10% Cu doping, the Cu10 sample becomes a Mott insulator effectively. These localized electrons partly contribute to the fluctuating magnetic moments, resulting in an enhancement in the effective magnetic moment as well as the local spin. Since the magnetic excitations around (0.5, 0.5) are not only present but also enhanced when the system is already in the insulating state, these excitations must not be purely resulting from the Fermi surface nesting as in a weak-coupling picture, otherwise they should be diminishing in Cu10. This is in line
considering the contributions from both components as transition-metal compounds, while both the itinerant-electron and local-moment picture have their own merits or drawbacks, a more appropriate approach seems to be considering the contributions from both components as well as the interactions between them.

Overall, our results indicate that the rigid-band shift model is not universally applicable in describing the substitution effect. One of the ingredients that needs to be taken into account is the different scattering potentials of the dopants. For example, from Co to Ni and to Cu, the scattering potential of the element is increasing. As a result, the suppression on the superconductivity and enhancement on the low-energy magnetic excitations become more significant. Another factor that makes the doping effect more complicated is the presence of multiple Fe $d$ orbitals. Because of their different characters, how they respond to the doping can also be different. Furthermore, Co, Ni, and Cu have roughly the same size, but Cu is Jahn Teller active and possibly can induce a different local distortion in the host lattice compared to Co and Ni (Ref. 57). Therefore, the Jahn Teller distortion can also play some role, which is to be examined with more detailed structural studies.

V. CONCLUSIONS

In summary, we have investigated the substitution effects of transition metal Cu in the iron-based superconductor Fe$_{0.98}$Te$_{0.5}$Se$_{0.5}$. It is found that, with 10\% Fe substituted by Cu atoms, the low-energy magnetic excitations up to $\sim$100 meV are significantly enhanced, while the high-energy spectra show negligible difference. The Cu substitution induces an enhancement of the effective moment from $2.85 \pm 0.06 \mu_B$/Fe in Cu$_{0}$ to $3.13 \pm 0.06 \mu_B$/Fe in Cu$_{10}$, which correspond to a spin of 1.01 $\pm$ 0.02 and 1.14 $\pm$ 0.02, respectively. The enhancement is at the cost of the itinerancy of the Fe electrons. These results depict the dual nature of magnetic excitations and interesting and complex doping effect beyond the rigid-band shift model in Fe$_{1+y-z}$Te$_{1-z}$Se$_{z}$ in specific, and likely in iron-based superconductors in general.

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1. M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, “Magnetic, transport, and optical properties of monolayer copper oxides,” Rev. Mod. Phys. 70, 897–928 (1998).
2. J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, “Evidence for stripe correlations of spins and holes in copper oxide superconductors,” Nature 375, 561–563 (1995).
3. J. M. Tranquada, H. Woo, T. G. Perring, H. Goka, G. D. Gu, G. Xu, M. Fujita, and K. Yamada, “Quantum magnetic excitations from stripes in copper oxide superconductors,” Nature 429, 534–538 (2004).
4. Pengcheng Dai, Jiangping Hu, and Elbio Dagotto, “Magnetism and its microscopic origin in iron-based high-temperature superconductors,” Nat. Phys. 8, 709–718 (2012).
5. Pengcheng Dai, “Antiferromagnetic order and spin dynamics in iron-based superconductors,” Rev. Mod. Phys. 87, 855–896 (2015).
6. John M. Tranquada, Guangyong Xu, and Igor A. Zaliznyak, “Superconductivity, antiferromagnetism, and neutron scattering,” J. Magn. Magn. Mater. 350, 148–160.
Qimiao Si, Rong Yu, and Elihu Abrahams, “High-temperature superconductivity in iron pnictides and chalcogenides.” Nat. Rev. Mater. 1, 16017 (2016)

S. Nandi, M. G. Kim, A. Kreyssig, R. M. Fernandes, D. K. Pratt, A. Thaler, N. Ni, S. L. Bud’ko, P. C. Canfield, J. Schmalian, R. J. McQueeney, and A. I. Goldman, “Anomalous Suppression of the Orthorhombic Lattice Distortion in Superconducting Ba(Fe1-xCo_x)2As2 Single Crystals,” Phys. Rev. Lett. 104, 057006 (2010)

Xingye Lu, H. Gretarsson, Rui Zhang, Xiongrou Liu, Huiqian Luo, Wei Tian, Mark Laver, Z. Yamani, Young-June Kim, A. H. Nevidomskyy, Qimiao Si, and Pengcheng Dai, “Avoided Quantum Criticality and Magnetoelectric Coupling in BaFe2-xNixAs2,” Phys. Rev. Lett. 110, 257001 (2013)

A. D. Christianson, E. A. Goremychkin, R. Osborn, S. Rosenkranz, M. D. Lumsden, C. D. Malliakas, I. S. Todorov, H. Claus, D. Y. Chung, M. G. Kanatzidis, R. I. Bewley, and T. Guidi, “Unconventional superconductivity in Ba0.6K0.4Fe2As2 from inelastic neutron scattering,” Nature 456, 930–932 (2008)

Shin-ichi Shimoto, Motoyuki Ishikado, Andrew D. Christianson, Mark D. Lumsden, Shuichi Wakimoto, Katsuaki Kodama, Akira Iyo, and Masatoshi Arao, “Inelastic neutron scattering study of the resonance mode in the optimally doped pnictide superconductor LaFeAsO9.92F0.08,” Phys. Rev. B 82, 172508 (2010)

Shiliang Li, Ying Chen, Sung Chang, Jeffrey W. Lynn, Liun-Ji Li, Yongkang Luo, Guanghan Cao, Zhu’an Xu, and Pengcheng Dai, “Spin gap and magnetic resonance in superconducting BaFe1.95Ni0.05As2,” Phys. Rev. B 79, 174527 (2009)

D. S. Inosov, J. T. Park, P. Bourges, D. L. Sun, Y. Sidis, A. Schneewind, K. Hradil, D. Haug, C. T. Lin, B. Keimer, and V. Hinkov, “Normal-state spin dynamics and temperature-dependent spin-resonance energy in optimally doped BaFe1.95Co0.05As2,” Nat. Phys. 6, 178–181 (2010)

Chang Liu, A. D. Pelczewski, R. S. Dhaka, Takeshi Kondo, R. M. Fernandes, E. D. Mun, H. Hodovanets, A. N. Thaler, J. Schmalian, S. L. Bud’ko, P. C. Canfield, and A. Kaminski, “Importance of the Fermi-surface topology to the superconducting state of the electron-doped pnictide Ba(Fe1-xCo_x)2As2,” Phys. Rev. B 84, 020509 (2011)

P. C. Canfield, S. L. Bud’ko, Ni Ni, J. Q. Yan, and A. Kracher, “Decoupling of the superconducting and magnetic/structural phase transitions in electron-doped BaFe2As2,” Phys. Rev. B 80, 060501 (2009)

M. Neupane, P. Richard, Y.-M. Xu, K. Nakayama, T. Sato, T. Takahashi, A. V. Fedorov, G. Xu, X. Dai, Z. Fang, Z. Wang, G.-F. Chen, N.-L. Wang, H.-W. Wen, and H. Ding, “Electron-hole asymmetry in the superconductivity of doped BaFe2As2 seen via the rigid chemical-potential shift in photoemission,” Phys. Rev. B 83, 094522 (2011)

Kazuma Nakamura, Ryotaro Arita, and Hiroaki Ikeda, “First-principles calculations of transition-metal-substituted iron pnictides,” Phys. Rev. Lett. 105, 157004 (2010)

Tom Berlijn, Chia-Hui Lin, William Garber, and Wei Ku, “Do Transition-Metal Substitutions Dope Carriers in Iron-Based Superconductors?” Phys. Rev. Lett. 108, 207003 (2012)

E. M. Bittar, C. Adriano, T. M. Garitezi, P. F. S. Rosa, L. Mendonça Ferreira, F. Garcia, G. de M. Azevedo, P. G. Pagliuso, and E. Granado, “Co-Substitution Effects on the Fe Valence in the BaFe2As2 Superconducting Compound: A Study of Hard X-Ray Absorption Spectroscopy,” Phys. Rev. Lett. 107, 267402 (2011)

M. G. Kim, J. Lamsal, T. W. Heitmann, G. S. Tucker, D. K. Pratt, S. N. Khan, Y. B. Lee, A. Alam, A. Thaler, N. Ni, S. Ran, S. L. Bud’ko, K. J. Marty, M. D. Lumsden, P. C. Canfield, B. N. Harmon, D. D. Johnson, A. Kreyssig, R. J. McQueeney, and A. I. Goldman, “Effects of Transition Metal Substitutions on the Incommensurability and Spin Fluctuations in BaFe2As2 by Elastic and Inelastic Neutron Scattering,” Phys. Rev. Lett. 109, 167003 (2012)

J. Li, Y. F. Guo, S. B. Zhang, J. Yuan, Y. Tsujimoto, X. Wang, C. I. Sathish, Y. Sun, S. Yu, W. Yi, K. Yamamura, E. Takayama-Muramachi, Y. Shirako, M. Akaogi, and H. Kontani, “Superconductivity suppression of Ba0.5K0.5Fe2−xM2xAs2 single crystals by substitution of transition metal (M = Mn, Ru, Co, Ni, Cu, and Zn),” Phys. Rev. B 85, 214509 (2012)

Jun Li, Jie Yuan, Min Ji, Guifei Zhang, Jun-Yi Ge, Hai-Luke Peng, Ya-Hua Yuan, Takeshi Hatano, Wei Hu, Kui Jin, Tobias Schwarz, Reinhold Kleiner, Dieter Koelle, Kazunari Yamamura, Hua-Bing Wang, Pei-Heng Wu, Ejji Takayama-Muramachi, Johan Vanacken, and Victor V. Meshchakov, “Impurity effects on the normal-state transport properties of Ba0.5K0.5Fe2As2 superconductors,” Phys. Rev. B 90, 024512 (2014)

Yizhou Xin, Ingrid Stolt, Yu Song, Pengcheng Dai, and W. P. Halperin, “Stripe antiferromagnetism and disorder in the Mott insulator NaFe2−xCuAs (x < 0.5),” Phys. Rev. B 101, 064410 (2020)

Yu Song, Zahra Yamani, Chongde Cao, Yu Li, Chenglin Zhang, Justin S. Chen, Qingzheng Huang, Hui Wu, Jing Tao, Yimei Zhu, Wei Tian, Songxue Chi, Huibo Cao, Yao-Bo Huang, Marcus Dantz, Thorsten Schmitt, Rong Yu, Andriy H. Nevidomskyy, Emilia Morosan, Qimiao Si, and Pengcheng Dai, “A Mott insulator continuously connected to iron pnictide superconductors,” Nat. Commun. 7, 13879 (2016)

Weiyi Wang, Yu Song, Ding Hu, Yu Li, Rui Zhang, L. W. Harriger, Wei Tian, Huibao Cao, and Pengcheng Dai, “Local breaking of fourfold rotational symmetry by short-range magnetic order in heavily overdoped Ba(Fe1−xCu)xAs2,” Phys. Rev. B 96, 161106 (2017)

Y. J. Yan, P. Cheng, J. J. Ying, X. G. Luo, F. Chen, H. Y. Zou, A. F. Wang, G. J. Ye, Z. J. Xiang, J. Q. Ma, and X. H. Chen, “Structural, magnetic, and electronic transport properties of hole-doped SrFe2−xCu,xAs2 single crystals,” Phys. Rev. B 87, 075105 (2013)

Yizhou Xin, Ingrid Stolt, Jeongseop A. Lee, Yu Song, Pengcheng Dai, and W. P. Halperin, “Toward the Mott state with magnetic cluster formation in heavily Cu-doped NaFe2−xCuAs,” Phys. Rev. B 99, 155114 (2019)

Yu Song, Weiyi Wang, Eugenio Paris, Xingye Lu, Jonathan Pelliciari, Yi Tseng, Yaobo Huang, Daniel McNally, Marcus Dantz, Chongde Cao, Rong Yu, Robert J. Birgeneau, Thorsten Schmitt, and Pengcheng Dai, “Spin dynamics in NaFeAs and NaFe0.53Cu0.47As probed by resonant inelastic x-ray scattering,” Phys. Rev. B 103, 075112 (2021)

Cun Ye, Wei Ruan, Peng Cai, Xintong Li, Aifeng Wang, Xianhui Chen, and Yayu Wang, “Strong Similarities be...
tween the Local Electronic Structure of Insulating Iron Pnictide and Lightly Doped Cuprate,” Phys. Rev. X 5, 021013 (2015).

Naoyuki Katayama, Sungdae Ji, Despina Louca, Seunghun Lee, Masaki Fujita, Taku J. Sato, Jinsheng Wen, Zhijun Xu, Genda Gu, Guangyong Xu, Ziwei Lin, Masanori Enoki, Sung Chang, Kazuyoshi Yamada, and John M. Tranquada, “Investigation of the Spin-Gridge Regime between the Antiferromagnetic and Superconducting Phases in Fe$_{1+y}$Se$_{1-x}$,” J. Phys. Soc. Jpn. 79, 113702 (2010).

J M Tranquada, Guangyong Xu, and I A Zaliznyak, “Magnetism and superconductivity in Fe$_{1+y}$Te$_{1-x}$,” J. Phys. Condens. Matter 32, 374003 (2020).

Jinsheng Wen, Zhijun Xu, Guangyong Xu, M. D. Lumsden, P. N. Valdivia, E. Bourret-Courchesne, Genda Gu, Dung-Hai Lee, J. M. Tranquada, and R. J. Birgeneau, “Magnetic order tuned by Cu substitution in Fe$_{1+1/4}$Cu$_{1/2}$,” Phys. Rev. B 86, 024401 (2012).

Hangdong Wang, Chiheng Dong, Zujuan Li, Jinhu Yang, Qianhui Mao, and Minghu Fang, “Evolution from antiferromagnetic order to spin-glass state in Fe$_{1+1/4}$Cu$_{1/2}$,” Phys. Lett. A 376, 3645–3648 (2012).

Tzu-Wen Huang, Ta-Kun Liu, Kuo-Wei Yeh, Chung-Ting Ke, Chi Liang Chen, Yi-Lin Huang, Fong-Chi Hsu, Maw-Kuen Wu, Phillip M. Wu, Maxim Avdeev, and Andrew J. Studer, “Doping-driven structural phase transition and loss of superconductivity in $\delta$Fe$_{1-\delta}$Se$_3$ ($M=Mn$, Cu),” Phys. Rev. B 82, 104502 (2010).

A J Williams, T M McQueen, V Ksenofontov, C Felser, and R J Cava, “The metal-insulator transition in Fe$_{0.01}$-Cu$_{0.75}$Se,” J. Phys. Condens. Matter 21, 305701 (2009).

Jinghui Wang, Ruidian Zhong, Shichao Li, Yuan Gan, Zhijun Xu, Cheng Zhang, T. Ozaki, M. Matsuda, Yang Zhao, Qianhui Mao, and Minghu Fang, “Evolution of the itinerant FeTe$_{0.95}$Te$_{0.55}$Se$_{0.5}$ depresses the normal-state conductivity but not the magnetic spectral weight,” Phys. Rev. B 91, 014501 (2015).

Jinsheng Wen, Shichao Li, Zhijun Xu, Cheng Zhang, M. Matsuda, O. Sobolev, J. T. Park, A. D. Christianson, E. Bourret-Courchesne, Qiang Li, Genda Gu, Dung-Hai Lee, J. M. Tranquada, Guangyong Xu, and R. J. Birgeneau, “Enhanced low-energy magnetic excitations via suppression of the itinerancy in Fe$_{0.08-0.1}$Cu$_{0.72}$Te$_{0.5}$Se$_{0.5}$,” Phys. Rev. B 88, 144509 (2013).

Yiming Qiu, Wei Bao, Y. Zhao, Collin Broholm, V. Stanev, Z. Tesanovic, Y. C. Gasparovic, S. Chang, Jin Hu, Bin Qian, Minghu Fang, and Zhiqiang Mao, “Spin Gap and Resonance at the Nesting Wave Vector in Superconducting FeSe$_{0.8}$Te$_{0.2}$,” Phys. Rev. Lett. 103, 067008 (2009).

T. J. Liu, J. Hu, B. Qian, D. Fobes, Z. Q. Mao, W. Bao, M. Reehuis, S. J. A. Kimber, K. Prokes, S. Matas, D. N. Argyriou, A. Hiess, A. Rotaru, H. Pham, L. Spinu, Y. Qiu, V. Thampy, A. T. Savici, J. A. Rodriguez, and C. Broholm, “From ($\pi$, $\pi$) magnetic order to superconductivity with ($\pi$, $\pi$) magnetic resonance in Fe$_{1.02}$Te$_{1-2\delta}$,” Nat. Mater. 9, 716–720 (2010).

D. N. Argyriou, A. Hiess, A. Akbari, I. Eremin, M. M. Korshunov, Jin Hu, Bin Qian, Zhiqiang Mao, Yiming Qiu, Collin Broholm, and W. Bao, “Incommensurate itinerant antiferromagnetic excitations and spin resonance in the FeTe$_{0.6}$Se$_{0.4}$ superconductor,” Phys. Rev. B 81, 220503 (2010).

P J Hirschfeld, M M Korshunov, and I I Mazin, “Gap symmetry and structure of Fe-based superconductors,” Rep. Prog. Phys. 74, 124508 (2011).

Igor I. Mazin, “Superconductivity gets an iron boost,” Nature 464, 183–186 (2010).

M. D. Lumsden, A. D. Christianson, E. A. Goremychkin, S. E. Nagler, H. A. Mook, M. B. Stone, D. L. Abernathy, T. Guidi, G. J. MacDougall, C. de la Cruz, A. S. Sefat, M. A. McGuire, B. C. Sales, and D. Mandrus, “Evolution of spin excitations into the superconducting state in FeTe$_1-x$Se$_x$,” Nat. Phys. 6, 182–186 (2010).

Guangyong Xu, Zhijun Xu, and J. M. Tranquada, “Absolute cross-section normalization of magnetic neutron scattering data,” Rev. Sci. Instrum. 84, 083906 (2013).

O. J. Lipscombe, G. F. Chen, Chen Fang, T. G. Perdew, D. L. Abernathy, A. D. Christianson, Takeshi Egami, Nanlin Wang, Jiangping Hu, and Pengcheng Dai, “Spin Waves in the ($\pi$, 0) Magnetically Ordered Iron Chalcogenide Fe$_{1+1/4}$Te,” Phys. Rev. Lett. 106, 057004 (2011).

C. Stock, E. E. Rodriguez, O. Sobolev, J. A. Rodriguez-Rivera, R. A. Ewings, J. W. Taylor, A. D. Christianson, and M. A.Green, “Soft striped magnetic fluctuations competing with superconductivity in Fe$_{1+1/4}$Te,” Phys. Rev. B 90, 121113 (2014).

Igor A. Zaliznyak, Zhijun Xu, John M. Tranquada, Genda Gu, Alexei M. Tsvelik, and Matthew B. Stone, “Unconventional temperature enhanced magnetism in Fe$_{1+1/4}$Te,” Phys. Rev. Lett. 107, 216403 (2011).

Meng Wang, Chenglin Zhang, Xingye Lu, Guotai Tan, Huiqian Luo, Yu Song, Miaoqiang Wang, Xiaotian Zhang, E. A. Goremychkin, T. G. Perring, T. A. Maier, Zhiping Yin, Kristjan Haule, Gabriel Kotliar, and Pengcheng Dai, “Doping dependence of spin excitations and its correlations with high-temperature superconductivity in iron pnictides,” Nat. Commun. 4, 2874 (2013).

Mengshi Liu, Leland W. Harriger, Huiqian Luo, Meng Wang, R. A. Ewings, T. Guidi, Hyowon Park, Kristjan Haule, Gabriel Kotliar, S. M. Hayden, and Pengcheng Dai, “Nature of magnetic excitations in superconducting BaFe$_{1.9}$Ni$_{0.1}$As$_2$,” Nat. Phys. 8, 376–381 (2012).

Qisi Wang, Yao Shen, Bingying Pan, Xiaowen Zhang, K. Ikeuchi, K. Iida, A. D. Christianson, H. C. Walker, D. T. Adroja, M. Abdel-Hafiez, Xiaojia Chen, D. A. Chareev, A. N. Vasiliev, and Jun Zhao, “Magnetic ground state of FeSe,” Nat. Commun. 7, 12182 (2016).

V. Cvetkovic and Z. Tesanovic, “Multiband magnetism and superconductivity in Fe-based compounds,” Europhys. Lett. 85, 37002 (2009).

Samuel Ducmatian, Rafael M. Fernandes, and Natalia B. Perkins, “Theory of the evolution of magnetic order in Fe$_{1+y}$Te compounds with increasing interstitial iron,” Phys. Rev. B 90, 165123 (2014).

Jiasheng Wu, Philip Phillips, and A. H. Castro Neto, “Theory of the Magnetic Moment in Iron Pnictides,” Phys. Rev. Lett. 101, 126401 (2008).

Song Bao, Wei Wang, Yanyan Shangguan, Zhengwei Cai, Zhao-Yang Dong, Zhentao Huang, Wenda Si, Zhen Ma, Ryoichi Kajimoto, Kazuhiko Ikeuchi, Shin-ichiro Yano, and Ryoichi Kajimoto, “Neutron Spectroscopy Evidence on the Dual Nature of Magnetic Excitations in a van der Waals Metallic Ferromagnet Fe$_{2.75}$GeTe$_3$,” Phys. Rev. X 12, 011022 (2022).

Younsik Kim, Minsoo Kim, Min-Seok Kim, Cheng-Maw Cheng, Joonyoung Choi, Saegyeol Jung, Donghui Lu,
Jong Hyuk Kim, Soohyun Cho, Dongjoon Song, Dongjin Oh, Li Yu, Young Jai Choi, Hyeong-Do Kim, Jung Hoon Han, Youn Jung Jo, Jungpil Seo, Soonsang Huh, and Changyoung Kim, “Kondo interaction in FeTe and its potential role in the magnetic order,” arXiv:2203.06432 (2022).

J. Georg Bednorz and K. Alex Müller, “Perovskite-type oxides—The new approach to high-$T_c$ superconductivity,” Rev. Mod. Phys. 60, 585 (1988).