Spin excitations in hole-overdoped iron-based superconductors

K. Horigane1, K. Kihou2, K. Fujita3, R. Kajimoto4, K. Ikeuchi5, S. Ji6, J. Akimitsu7 & C. H. Lee2

Understanding the overall features of magnetic excitation is essential for clarifying the mechanism of Cooper pair formation in iron-based superconductors. In particular, clarifying the relationship between magnetism and superconductivity is a central challenge because magnetism may play a key role in their exotic superconductivity. BaFe2As2 is one of ideal systems for such investigation because its superconductivity can be induced in several ways, allowing a comparative examination. Here we report a study on the spin fluctuations of the hole-overdoped iron-based superconductors Ba1-xKxFe2As2 (x = 0.5 and 1.0; Tc = 36 K and 3.4 K, respectively) over the entire Brillouin zone using inelastic neutron scattering. We find that their spin spectra consist of spin wave and chimney-like dispersions. The chimney-like dispersion can be attributed to the itinerant character of magnetism. The band width of the spin wave-like dispersion is almost constant from the non-doped to optimum-doped region, which is followed by a large reduction in the overdoped region. This suggests that the superconductivity is suppressed by the reduction of magnetic exchange couplings, indicating a strong relationship between magnetism and superconductivity in iron-based superconductors.

Spin-mediated superconductivity is one of the plausible models explaining the formation of Cooper pairs in iron-based superconductors. To investigate this hypothesis, magnetism has been intensively studied. The neutron scattering technique is a powerful method of examining spin fluctuations, because it can clarify both the energy and momentum dependences over the entire Brillouin zone. Revealing the overall spectrum of spin fluctuation is essential for understanding their magnetism and the mechanism of spin-mediated superconductivity.

The magnetism dependence of superconductivity should be demonstrated to prove that the superconductivity is due to spin fluctuations. AFe2As2 (A = Ba, Sr or Ca) is one of ideal systems for this purpose, because its superconductivity can be induced in several ways: electron doping1-2, hole doping3, chemical pressure4 and external pressure5. Systematic and comparative studies among those samples can solve the problem.

The antiferromagnetic (AF) long-range ordering commonly observed in the parent compounds disappears and Tc increases by applying pressure or upon doping in the underdoped region5-6. Apparently, AF long-range ordering competes against superconductivity. In the overdoped region, on the other hand, it is unclear why Tc decreases and the superconductivity disappears with increasing doping. Inelastic neutron scattering (INS) studies on electron-doped Ba(Fe,Ni)2As2 have clarified that the spin fluctuations at high-energy region (>100 meV) are insensitive to doping5 whereas those at low-energy region (<50 meV) disappear as Tc decreases in the overdoped region5. It has been demonstrated that low-energy spin fluctuations are correlated with superconductivity. For hole-doped (Ba,K)Fe2As2, on the other hand, low-energy spin fluctuations remain even in heavily overdoped KFe2As2 below E = 20 meV5-6. Thus, why Tc decreases upon hole doping in the hole-overdoped region remains as an unanswered question.

INS studies on the spin fluctuations of non-doped AFe2As2 (A = Ba, Sr or Ca) over the entire Brillouin zone have clarified that the spin dispersion can be well described by the J1-J2 model. However, it is unclear whether the model, which is based on a localized spin picture, is valid because carriers show an itinerant character. In fact,
many calculations based on itinerant models have been proposed to explain the spin spectra\textsuperscript{10–12}. Some models, for example based on the combination of density functional theory and dynamical mean-field theory, attempt to involve both itinerant and localized characters\textsuperscript{13,14}. To establish a definitive model of magnetism, further examination of spin fluctuations is required.

Although systematic studies on spin fluctuations of electron-doped Ba(Fe,Ni)\textsubscript{2}As\textsubscript{2} have been reported\textsuperscript{7,15}, the spin fluctuations of hole-overdoped samples over the entire Brillouin zone have not yet been established. In previous INS experiments on KFe\textsubscript{2}As\textsubscript{2}, spin fluctuations were observed up to \(E = 20\) meV, which is halfway to the zone boundary\textsuperscript{8,9}. In optimum-doped (Ba,K)Fe\textsubscript{2}As\textsubscript{2}, a conflict between INS and resonant x-ray inelastic scattering (RIXS) has been found. The spin dispersion is robust upon doping according to the results of INS\textsuperscript{8} whereas softening has been observed in RIXS experiments\textsuperscript{16}. To solve this problem, further study of the hole doping dependence is essential. We, thus, report the overall spectra of spin fluctuations in overdoped Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) obtained by the INS technique.

Results
Figure 1(a–e) show the observed two-dimensional constant-energy images of spin excitations in the case of Ba\(_{0.5}\)K\(_{0.5}\)Fe\(_2\)As\(_2\). Figure 1(f–j) show the results of calculations with peak positions derived from the Gaussian fitting of constant-energy spectra. We describe the (H, K) plane with orthorhombic notation, even though superconducting Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) has a tetragonal crystal structure to facilitate comparison with non-doped BaFe\(_2\)As\(_2\).
Clear incommensurate peaks appeared around the \((\pm 1, 0)\) and \((0, \pm 1)\) splitting along the longitudinal direction with a wave vector of \((\pm 2\delta, 0)\) and \((0, \pm 2\delta)\), respectively, where \(\delta = 0.06\) at \(E = 13\) meV. The \((\pm 1, &pm; 2\delta, 0)\) position corresponds to \([\pi (1 \pm 2\delta, 0)]\) in the ab plane and \((0.5 \pm \delta, 0.5 \pm \delta)\) in tetragonal notation. As the energy increases, spin excitations start to split along the transverse direction corresponding to \((\pm 1 \pm 2\delta, K)\) or \((H, \pm 1 \pm 2\delta)\) and reach the magnetic zone boundary with merging signals from next zone boundaries. In contrast, magnetic excitations along the longitudinal direction corresponding to \((\pm 1 \pm 2\delta + H, 0)\) or \((0, \pm 1 \pm 2\delta + K)\) are strongly damped, consistent with previous observations for the BaFe\(_2\)As\(_2\) system\(^{17}\). Figure 1(k,l) show the dispersion cuts along the transverse direction \((1, K)\). A clear spin wave-like dispersion was observed up to \(E = 200\) meV, where it reaches the zone boundary.

Figure 2(a–j) show two-dimensional constant-energy images of spin excitations and the results of calculations for \(x = 1\). Well-defined incommensurate peaks with incommensurability larger than that for \(x = 0.5\) are observed at \(E = 5\) meV. With increasing energy, spin excitations split along the transverse direction, similarly to the case of \(x = 0.5\). The dispersion cut along the transverse direction \((0.68, K)\) shows that the spin excitations reach the zone boundary around \(E = 80\) meV (Fig. 2(k)). Nevertheless, magnetic signals exist even considerably above \(E = 80\) meV with a vertical dispersion exhibiting a chimney-like structure (Fig. 2(l,m)). The energy-constant cuts along the \(K\) direction clearly show that the magnetic signals extend up to \(E \sim 200\) meV (Fig. 2(m)).
Next, we overview the overall spin dispersion of Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\). Figure 3(a–c) show the spin excitation dispersions for \(x = 0.5\) and 1 at \(T = 6\) K derived from Gaussian fitting of the constant-energy spectra with those of the non- and underdoped samples. In \(x = 0.5\), a spin wave dispersion is observed up to \(E = 200\) meV, similarly to the cases of \(x = 0\) and 0.33 (Fig. 3(a)). In \(x = 1\), on the other hand, the dispersive spin excitations reach the zone boundary around \(E = 80\) meV, which is considerably lower than the energy for \(x = 0.5\) (Fig. 3(b)). Instead, a vertical dispersion with a chimney-like structure was observed from \(E = 80\) meV up to 200 meV. In \(x = 0.5\), signals of the chimney-like structure can also be found above \(E = 200\) meV, but they are less clear than those in \(x = 1\) (Fig. 3(m)).

Figure 3(d) shows the energy dependence of the dynamical magnetic susceptibility \(\int \chi''(q, \omega) dq\) for \(x = 0.5\) and 1 at \(T = 6\) K derived from Gaussian fitting of the constant-energy spectra with those of the non- and underdoped samples. In \(x = 0.5\), a spin wave dispersion is observed up to \(E = 200\) meV, similarly to the cases of \(x = 0\) and 0.33 (Fig. 3(a)). In \(x = 1\), on the other hand, the dispersive spin excitations reach the zone boundary around \(E = 80\) meV, which is considerably lower than the energy for \(x = 0.5\) (Fig. 3(b)). Instead, a vertical dispersion with a chimney-like structure was observed from \(E = 80\) meV up to 200 meV. In \(x = 0.5\), signals of the chimney-like structure can also be found above \(E = 200\) meV, but they are less clear than those in \(x = 1\) (Fig. 1(m)).

Figure 3(d) shows the energy dependence of the dynamical magnetic susceptibility \(\int \chi''(q, \omega) dq\) for \(x = 0.5\) and 1 at \(T = 6\) K. \(\int \chi''(q, \omega) dq\) for \(x = 0, 0.33, 0.5, 1\) at \(T = 38.5\) K and BaFe\(_2\)As\(_2\) \((y = 0.18, T_c = 8\) K) reported in\(^{7,8}\) are also depicted for comparison. It can be seen that \(\int \chi''(q, \omega) dq\) for \(x = 0.5\) exhibits essentially equivalent behavior to that for \(x = 0.33\). Compared with the case of \(x = 0\), on the other hand, the signals in the high-energy region are much lower for \(x = 0.5\), while the peak energy remains around \(E = 150–200\) meV. For \(x = 1\), \(\int \chi''(q, \omega) dq\) above \(E = 100\) meV is further low, with the peak energy decreasing to around \(E = 30\) meV. The large reduction in the high-energy spin fluctuations with hole doping results in suppression of the total fluctuating moment, which has been estimated to be \(<m^2> = 1.45\) and \(0.65 \mu_B^2/\text{Fe}\), for \(x = 0.5\) and 1, respectively (Fig. 4). In contrast, \(\int \chi''(q, \omega) dq\) in the low-energy region is almost independent of the doping level except for the sharp peak attributed to the spin resonance. Thus, the suppression of superconductivity in the hole-overdoped region cannot be due to a decrease in low-energy magnetic intensity as for electron-doped Ba(Fe,Ni)\(_2\)As\(_2\).\(^{7,8}\)

**Discussion**

The present observations demonstrate that the energy scale of the dispersive spin wave is robust upon hole doping up to \(x = 0.5\), which is followed by a rapid decrease up to \(x = 1\) (Fig. 4). The decrease appears to be related to the appearance of the incommensurate spin structure. In fact, the band width is robust in electron-doped
Ba(Fe,Co,Ni)2As2, which exhibits a commensurate spin structure except in the incommensurate AF state, which appears in a narrow doping range and has one-order smaller incommensurability than that of KFe2As2. The smaller band width of the spin wave leads to weaker effective magnetic exchange coupling \( J \) according to the Heisenberg model. The results, thus, suggest that \( J \) is correlated with the periodicity of spin fluctuations. The small value of \( J \) in KFe2As2 is consistent with the fact that its electronic interaction strength \( U \) is quite large.

The chimney-like structure can originate from particle-hole excitations, which define the itinerant character of spin fluctuations. Note that the chimney-like structure resembles the spin excitations in the itinerant AF metals Cr21, Cr0.95V0.0522 and Mn2AsFe2Si23. The present results show that the band width decreases and the chimney-like dispersion appears with hole doping. This is qualitatively consistent with DFT + DMFT calculations13,14, which also supports the origin of the chimney-like dispersion to be particle-hole excitations.

The present observation of a large reduction in high-energy spin fluctuations upon hole doping is in contrast to the case of electron-doped Ba(Fe,Ni)2As2, where high-energy spin fluctuations are independent of doping. Because hole-doped (Ba,K)Fe2As2 exhibits a higher maximum \( T_c \) of 38 K than electron-doped Ba(Fe,Ni)2As2 \( (T_c = 20 \text{ K}) \) even though (Ba,K)Fe2As2 exhibits weaker spin fluctuations in the high-energy region, this reduction of the high-energy spin fluctuations does not appear to suppress \( T_c \). The suppression of \( T_c \) in hole-overdoped (Ba,K)Fe2As2 can rather be attributed to the reduction of \( J \), which remains almost constant from non-doped to optimum-doped region and followed by rapid reduction in the overdoped region. The \( J \) dependence of the superconductivity has also been suggested in studies on spin resonance24–26. Stronger magnetic correlation leads to a larger energy split between the resonance and the superconducting gap energy. In fact, the resonance energy in overdoped (Ba,K)Fe2As2 approaches the superconducting gap energy with doping up to \( x = 0.77 \)24, which can result from the reduction of \( J \). These results lead to the conclusion that there is a strong relationship between magnetism and superconductivity in Ba1-xKxFe2As2.

**Method**

Single crystals of Ba0.5K0.5Fe2As2 \( (T_c = 36 \text{ K}) \) and KFe2As2 \( (T_c = 3.4 \text{ K}) \) were grown by a KAs self-flux method27,28. The magnetic susceptibility was measured by a SQUID from Quantum Design. The INS measurement was performed using the Fermi chopper spectrometer 4SEASONS in J-PARC29. We co-aligned 160 and 300 pieces of single crystal with \( x = 0.5 \pm 0.5 \) g and \( x = 1 \pm 0.5 \) g, respectively. We employed the multi-\( E_i \) method30 with incident neutron energies of \( E_i = 31, 65, 110, 202, 409, 720 \text{ meV} \) for Ba0.5K0.5Fe2As2 and \( E_i = 30, 75, 149, 423 \text{ meV} \) for KFe2As2. The incident beam was parallel to the c-axis. We converted signal intensities into absolute units using a vanadium standard. The data were processed by the “Utsusemi” visualization software developed at J-PARCC1. Throughout this letter, wave vectors are specified in the orthorhombic reciprocal lattice.

**References**

1. A. S. Sefat et al. Superconductivity at 22 K in Co-doped BaFe2As2 crystals. *Phys. Rev. Lett.* **101**, 117004 (2008).
2. L. J. Li et al. Superconductivity induced by Ni doping in BaFe2As2 single crystals. *New J. Phys.* **11**, 025008 (2009).
3. M. Rotter, M. Tegel & D. Johrendt. Superconductivity at 38 K in the iron arsenide (Ba1-xKx)Fe2As2. *Phys. Rev. Lett.* **101**, 107006 (2008).
4. S. Jiang et al. Superconductivity up to 30K in the vicinity of quantum critical point in BaFe1-xKxAs2. *J. Phys.: Condens. Matter* **21**, 382203 (2009).
5. P. L. Alireza et al. Superconductivity up to 29 K in SrFe2As2 and BaFe2As2 at high pressures. *J. Phys.: Condens. Matter* **21**, 012208 (2009).
6. S. Avci et al. Phase diagram of Ba1-xKxFe2As2. *Phys. Rev. B* **85**, 184507 (2012).
7. H. Luo et al. Electron doping evolution of the magnetic excitations in BaFe1-xNi2As2. *Phys. Rev. B* **88**, 144516 (2013).
8. M. Wang et al. Doping dependence of spin excitations and its correlations with high-temperature superconductivity in iron pnictides. *Nat. Commun.* **4**, 2874 (2013).
9. C. H. Lee et al. Incommensurate spin fluctuations in hole-overdoped superconductor KFe2As2. *Phys. Rev. Lett.* **106**, 067003 (2011).
10. J. Knolle, I. Eremin, A. V. Chubukov & R. Moessner. Theory of itinerant magnetic excitations in the spin-density-wave phase of iron-based superconductors. *Phys. Rev. B* **81**, 140506(R) (2010).
11. E. Kaneshita & T. Tohyama. Spin and charge dynamics ruled by antiferromagnetic order in iron pnictide superconductors. *Phys. Rev. B* **82**, 094441 (2010).
12. M. Kovacic, M. H. Christensen, M. N. Gastiasoro & B. M. Andersen. Spin excitations in the nematic phase and the metallic stripe spin-density wave phase of iron pnictides. *Phys. Rev. B* **91**, 064424 (2015).
13. H. Park, K. Haule & G. Kotliar. Magnetic excitation spectra in BaFe$_2$As$_2$: a two-particle approach within a combination of the density functional theory and the dynamical mean-field theory method. *Phys. Rev. Lett.* **107**, 137007 (2011).
14. Z. P. Yin, K. Haule & G. Kotliar. Spin dynamics and orbital-antiphase pairing symmetry in iron-based superconductors. *Nat. Phys.* **10**, 845 (2014).
15. M. Liu et al. Nature of magnetic excitations in superconducting BaFe$_2$As$_2$. *Nat. Phys.* **8**, 376 (2012).
16. K.-J. Zhou et al. Persistent high-energy spin excitations in iron-pnictide superconductors. *Nat. Commun.* **4**, 1470 (2013).
17. L. W. Harriger et al. Nematic spin fluid in the tetragonal phase of BaFe$_2$As$_2$. *Phys. Rev. B* **84**, 054544 (2011).
18. D. K. Pratt et al. Incommensurate spin-density wave order in electron-doped BaFe$_2$As$_2$ superconductors. *Phys. Rev. Lett.* **106**, 257001 (2011).
19. H. Fukazawa et al. NMR/NQR and specific heat studies of iron pnictide superconductor KFe$_2$As$_2$. *J. Phys. Soc. Jpn.* **80**, SA118 (2011).
20. F. Hardy et al. Evidence of strong correlations and coherence-incoherence crossover in the iron pnictide superconductor KFe$_2$As$_2$. *Phys. Rev. Lett.* **111**, 027002 (2013).
21. Y. Endoh & P. Böni. Magnetic excitations in metallic ferro- and antiferromagnets. *J. Phys. Soc. Jpn.* **75**, 111002 (2006).
22. S. M. Hayden et al. Strongly enhanced magnetic excitations near the quantum critical point of Cr$_{1-x}$V$_x$ and why strong exchange enhancement need no imply heavy fermion behavior. *Phys. Rev. Lett.* **84**, 999 (2000).
23. S. Tomiyoshi et al. Magnetic excitations in the itinerant antiferromagnets Mn$_3$Si and Fe-doped Mn$_3$Si. *Phys. Rev. B* **36**, 2181 (1987).
24. C. H. Lee et al. Suppression of spin-exciton state in hole overdoped iron-based superconductors. *Sci. Rep.* **6**, 23424 (2016).
25. C. H. Lee et al. Universality of the dispersive spin-resonance mode in superconducting BaFe$_2$As$_2$. *Phys. Rev. Lett.* **111**, 167002 (2013).
26. D. K. Pratt et al. Dispersion of the superconducting spin resonance in underdoped and antiferromagnetic BaFe$_2$As$_2$. *Phys. Rev. B* **81**, 140510(R) (2010).
27. K. Kihou et al. Single crystal growth and characterization of the iron-based superconductor KFe$_2$As$_2$, synthesized by KAs flux method. *J. Phys. Soc. Jpn.* **79**, 124713 (2010).
28. K. Kihou et al. Single-crystal growth of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ by KAs self-flux method. *J. Phys. Soc. Jpn.* **85**, 034718 (2016).
29. R. Kajimoto et al. The Fermi chopper spectrometer 4SEASONS at J-PARC. *J. Phys. Soc. Jpn.* **80**, SB025 (2011).
30. M. Nakamura et al. First demonstration of novel method for inelastic neutron scattering measurement utilizing multiple incident energies. *J. Phys. Soc. Jpn.* **78**, 093002 (2009).
31. Y. Inamura, T. Nakatani, J. Suzuki & T. Otomo. Development status of software “Utsusemi” for chopper spectrometers at MLF, J-PARC. *J. Phys. Soc. Jpn.* **82**, SA031 (2013).

**Acknowledgements**

We would like to acknowledge H. Hiraka, T. Fukuda, S. Onari, T. Tohyama and K. Yamada for valuable discussions. The neutron experiment at the Materials and Life Science Experimental Facility of J-PARC was performed under user programs (2012B0075 and 2013B0061). This work was supported by Grants-in-Aid for Scientific Research B (24340090, 25287081) and for Young Scientists B (16K17750) from Japan Society for the Promotion of Science.

**Author Contributions**

K.H., C.H.L., K.F., K.K. and S.J. conducted the inelastic neutron scattering measurements and analyzed the data. K.H., K.K. and K.F. synthesized and characterized the single crystals. C.H.L. and J.A. designed and coordinated the experiment. All authors contributed to and discussed the manuscript.

**Additional Information**

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Horigane, K. et al. Spin excitations in hole-overdoped iron-based superconductors. *Sci. Rep.* **6**, 33303; doi: 10.1038/srep33303 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2016