Title
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Permalink
https://escholarship.org/uc/item/5qp6z5k3

Journal
Physical Review B - Condensed Matter and Materials Physics, 92(4)

ISSN
1098-0121

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Publication Date
2015-07-13

DOI
10.1103/PhysRevB.92.041109

Peer reviewed
Spin Waves and Spatially Anisotropic Exchange Interactions in the S = 2 Stripe Antiferromagnet $\text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_{2}$

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An inelastic neutron scattering study of the spin waves corresponding to the stripe antiferromagnetic order in insulating $\text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_{2}$ throughout the Brillouin zone is reported. The spin wave spectra are well described by a Heisenberg Hamiltonian with anisotropic in-plane exchange interactions. Integrating the ordered moment and the spin fluctuations results in a total moment squared of $\mu_{B}^{2} = 27.3 \pm 2.5 \mu_{B}/\text{Fe}$, consistent with $S \approx 2$. Unlike $X\text{Fe}_{2}\text{As}_{2}$ ($X = \text{Ca}, \text{Sr},$ and $\text{Ba}$), where the itinerant electrons have a significant contribution, our data suggest that this stripe antiferromagnetically ordered phase in $\text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_{2}$ is a Mott-like insulator with fully localized 3$d$ electrons and a high-spin ground state configuration. Nevertheless, the anisotropic exchange couplings appear to be universal in the stripe phase of Fe pnictides and chalcogenides.

PACS numbers: 25.40.Fq, 75.30.Ds, 75.50.Ee, 78.70.Nx

Superconductivity emerges in the vicinity of antiferromagnetism (AFM) in both copper based and iron based high-transition temperature (high-$T_c$) superconductors\cite{1,2,3}. The AFM in these systems share several similarities: antiferromagnetic order in insulating rare-earth doped $\text{Ca}_{1-x}\text{Sr}_{x}\text{Fe}_{2}\text{As}_{2}$ throughout the Brillouin zone is reported. The spin wave spectra are well described by a Heisenberg Hamiltonian with anisotropic in-plane exchange interactions. Integrating the ordered moment and the spin fluctuations results in a total moment squared of $\mu_{B}^{2} = 27.3 \pm 2.5 \mu_{B}/\text{Fe}$, consistent with $S \approx 2$. Unlike $X\text{Fe}_{2}\text{As}_{2}$ ($X = \text{Ca}, \text{Sr},$ and $\text{Ba}$), where the itinerant electrons have a significant contribution, our data suggest that this stripe antiferromagnetically ordered phase in $\text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_{2}$ is a Mott-like insulator with fully localized 3$d$ electrons and a high-spin ground state configuration. Nevertheless, the anisotropic exchange couplings appear to be universal in the stripe phase of Fe pnictides and chalcogenides.

From a localized point of view, with 6 electrons in the iron 3$d$ orbitals of Fe$^{2+}$, the maximum total spin is $S = 2$. This spin state can be realized when the Hund’s Rule coupling energy, $J_H$, dominates over the crystal-field splitting associated with the FeM$_4$ ($M = \text{pnictigens or chalcogens}$) structural unit. On the other hand, a crystal-field splitting $\Delta_{\text{CF}}$ comparable to the Hund’s coupling $J_H$ can lead to an intermediate-spin $S = 1$ state. In the large crystal field extreme, the 3$d^6$ ions of Fe$^{2+}$ will form a low-spin singlet $S = 0$ state\cite{4,5}. In the presence of itinerant carriers the spin must be less than $S = 2$ due to charge fluctuations. Thus, while the observation of an intermediate-spin state $S = 1$ does not rule out the presence of itinerant carriers, the observation of $S = 2$ would require the system to be predominately localized. Not surprisingly, the various values of ordered moments observed in different iron-based materials have been interpreted in terms of both the local moment picture and the itinerant carrier picture\cite{6,7,8,9}. As to the value of the fluctuating local moment, inelastic neutron scattering experiments combined with the moment sum rule revealed an increase of $S$ from $S \approx 1 $ at 10 K to $S \approx 2/3$ at 300 K for Fe$_{1.1}$Te and a constant $S = 1/2$ for BaFe$_2$As$_2$\cite{10,11,12}. In addition, an X-ray emission spectroscopy study was interpreted to imply that the iron spin-state varied between $S = 0$ and 2 in the rare-earth doped Ca$_{1-x}$RE$_x$Fe$_2$As$_2$ as a function of temperature\cite{13}. In contrast, studies of the spin wave excitations in $X\text{Fe}_{2}\text{As}_{2}$ ($X = \text{Ca}, \text{Sr},$ and $\text{Ba}$) have found significant special weight contributions from both itinerant carriers and local moments\cite{14,15,16,17}. These findings suggest that the magnetism of the iron pnictides and chalcogenides should be understood from a point of view where both itinerant carriers and local moments coexist.

The substitution of sulfur for selenium progressively suppresses the superconductivity in $\text{K}_{0.8}\text{Fe}_{2}\text{Se}_{2-x}\text{S}_x$ and decreasing the Fe content results in an insulating ground state\cite{18,19}. We found a stripe AF order in insulat-
therefore important to characterize the spin waves asso-
ciated with the stripe AF order in Rb$_{0.8}$Fe$_{1.5}$S$_2$. We use the orthorhombic unit cell as shown by the solid square in (b) with lattice parameters of $a = 5.58 \text{ Å}, b = 5.39 \text{ Å},$ and $c = 13.889 \text{ Å}$. The wave vector $Q$ is defined as $Q = \{H, K, L\} = (2\pi H/a, 2\pi K/b, 2\pi L/c)$ in reciprocal lattice units (r.l.u.). The dashed rectangle is the real magnetic unit cell. (c) Dynamic susceptibility $\chi'(\omega)$ as a function of energy with $E_i = 35, 170,$ and $250 \text{ meV}$ at $8 \text{ K}$. The solid line is computed by the model discussed in the text. The dashed line is the dynamic susceptibility of BaFe$_2$As$_2$ from Ref. [12]. (d) A candidate for the high-spin ground state configuration of the stripe AF order[7].

![Figure 1](image)

FIG. 1: (color online) Three- (a) and Two- (b) dimensional structures of the stripe AF order with rhombic iron vacancy order in Rb$_{0.8}$Fe$_{1.5}$S$_2$. We use the orthorhombic unit cell as shown by the solid square in (b) with lattice parameters of $a = 5.58 \text{ Å}, b = 5.39 \text{ Å},$ and $c = 13.889 \text{ Å}$. The wave vector $Q$ is defined as $Q = \{H, K, L\} = (2\pi H/a, 2\pi K/b, 2\pi L/c)$ in reciprocal lattice units (r.l.u.). The dashed rectangle is the real magnetic unit cell. (c) Dynamic susceptibility $\chi'(\omega)$ as a function of energy with $E_i = 35, 170,$ and $250 \text{ meV}$ at $8 \text{ K}$. The solid line is computed by the model discussed in the text. The dashed line is the dynamic susceptibility of BaFe$_2$As$_2$ from Ref. [12]. (d) A candidate for the high-spin ground state configuration of the stripe AF order[7].

ing Rb$_{0.8}$Fe$_{1.5}$S$_2$ with a rhombic iron vacancy order and a strikingly similar Néel temperature of $T_N = 275 \text{ K}$ with a moment size of $M = 2.8 \pm 0.5\mu_B$ as that in K$_{0.8}$Fe$_{1.5}$Se$_2$[20, 21]. Photoemission measurements revealed a 980 meV charge gap in the rhombic iron vacancy ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22]. The stripe AF order was proposed as a candidate parent compound for the superconducting ordered phase[22].

We show spin excitations in the $[H, K]$ plane at various energies in Fig. 2 (a-e). The spin excitations stem from the AF wave vectors, disperse outwards and separate into two arcs at $E = 65 \pm 5$ and $75 \pm 5 \text{ meV}$. At the energy of $110 \pm 9 \text{ meV}$, the wave vectors rotate $90^\circ$. Weak spin excitations at $Q = (\pm 1 \pm 0.5, 0), (0, \pm 1 \pm 0.5)$ and $(\pm 1, \pm 1)$ in Fig. 2 (a) can also be observed.

To describe the spin waves in Rb$_{0.8}$Fe$_{1.5}$S$_2$, we employed a Heisenberg model with in-plane nearest-($J_{1a}$, $J_{1b}$), and next-nearest-($J_2$) neighbor exchange couplings, together with the coupling between layers, $J_c$, as shown in Fig. 1 (a) and Fig. 1 (b), and the single ion anisotropy term, $J_s$. The Hamiltonian can be written as:

$$
\hat{H} = \frac{J_{r,r'}}{2} \sum_{r,r'} \mathbf{S}_r \cdot \mathbf{S}_{r'} - J_s \sum_{r} (\mathbf{S}_r^2)^2,
$$

(1)

where $J_{r,r'}$ are the effective exchange couplings and $(r, r')$ label the iron sites[20]. The spin wave excitation spectrum can be expressed analytically by solving Eq. (1) using the linear spin wave approximation[13, 15, 17, 24]. We fit the data and convolute the instrumental resolution using the Tobyfit program[27]. From the best fit to the experimental data, we determine the parameters as $SJ_{1a} = 42 \pm 5, SJ_{1b} = -20 \pm 2,$ and $SJ_2 = 17 \pm 2 \text{ meV},$ and for computational convenience an energy independent damping $\Gamma = 7 \pm 2 \text{ meV}$. The widths of the spin
wave peaks in $H$ and $K$ were close to being instrumental resolution limited as expected for an insulator; this also holds true for $K_{0.81}\text{Fe}_{1.58}\text{Se}_{2}$ \cite{28, 29}. The simulations with the fit parameters at the identical energies of Fig. 2 (a-c) are presented in Fig. 2 (f-j).

To compare quantitatively the experimental data with the model, we plot cuts along the $[H,0]$ and $[1,K]$ directions for a wide range of energies in Fig. 3. The solid lines are the results of the best fits with the parameters discussed above. The fits are in good agreement with the experimental data at all energies. The small discrepancy between 90 and 120 meV in Fig. 4 (b) can be observed. The temperature dependent spin gap remained sharp right up to the phase transition. The scaled magnetic order parameter is plotted along with the temperature dependent spin gap. The evolution of the spin gap with temperature follows the trend of the AF order, in agreement with the behavior observed in $K_{2}\text{NiF}_4$, a quasi-two-dimensional (2D) Heisenberg AF insulator\cite{29}.

To unveil the spin state in the stripe AF order of $Rb_{0.8}\text{Fe}_{1.5}\text{S}_2$, we examined the sum rule of the magnetic neutron scattering. One can calculate the total fluctuating moment squared $\langle \mathbf{m}^2 \rangle$ by integrating the susceptibility $\chi''(\mathbf{q}, \omega)$ over the band width of the spin excitations via

$$\langle \mathbf{m}^2 \rangle = \frac{3\hbar}{\pi} \int_0^{+\infty} \int q d\omega \frac{\chi''(\omega)}{1 - \exp(-\hbar \omega/k_B T)} d\omega .$$

The total moment sum rule is $M_J^2 = g^2 M^2 + \langle \mathbf{m}^2 \rangle = g^2 S(S+1)$, where $g$ is the Landé $g$-factor and $S$ the total spin.
M is the static moment. Thus the spin S can be extracted [24] [39] [51].

The averaged dynamic susceptibility in a Brillouin zone \( \chi''(\omega) = \int \chi''(\mathbf{q}, \omega) d\mathbf{q} / \int d\mathbf{q} \) is plotted in Fig. 1 (c). The spin fluctuations in Rb\(_{0.8}\)Fe\(_{1.5}\)S\(_2\) are obviously stronger than those in BaFe\(_2\)As\(_2\). Integrating the dynamic susceptibility through all the spin excitation band width results in 29.7±5.5\(\mu_B^2\)/formula unit (f.u.), and thus 19.8±3.7\(\mu_B^2\)/Fe. Taking the ordered moment \( M = 2.8±0.5\mu_B \) into account \( M_B^2 = (2.8±0.5)^2 + (19.8±3.7)^2 \), the total moment squared per Fe is 27.6±4.2\(\mu_B^2\), which assuming \( g = 2.0 \) results in a spin \( S = 2.2±0.2 \), which is equal to the upper limit of 24\(\mu_B^2\) and \( S = 2 \) as the Hund’s rule result for the 3\textit{d} \textit{Fe}\(^{2+} \) within the error. The results reveal that to within the errors all six 3\textit{d} electrons of Fe\(^{2+} \) are associated with the local moments and in the high-spin state. A candidate spin configuration is illustrated in Fig. 1 (d). The fact that the carriers are fully localized in Rb\(_{0.8}\)Fe\(_{1.5}\)S\(_2\) is consistent with our photoemission measurements on several pieces of single crystals from the same batch of nearly 100% stripe AF phase. These measurements also reveal a large charge gap below the Fermi energy, suggesting that the stripe AF phase is a Mott-like insulator with the integer spin \( S = 2 \) [23] [32], rather than a small gap band insulator [20] [21] [33]. The rhombic iron vacancy order stabilized at a longer in-plane Fe-Fe distance (2.750 Å) of the stripe AF order larger than that of the block AF order (2.663 Å) in Rb\(_{0.8}\)Fe\(_{1.5}\)S\(_2\) could enhance the correlation and thus promotes the localization [23] [32].

Several theoretical methods have been successfully explored to describe the spin waves of the stripe AF order: a combination of density functional theory (DFT) and dynamic mean field theory (DMFT) [34] [35]: a Heisenberg model with the anisotropic in-plane exchange couplings \( J_\text{1a}(>0), J_\text{1b}(<0), \) and \( J_\text{2} \) [36] [37] [38]: and a Heisenberg model with \( J_1, J_2 \) and a large biquadratic coupling \( K \) [10] [36] [37]. The origins of the anisotropy in the \( J_\text{1a} - J_\text{1b} - J_2 \) model and the large biquadratic coupling in the \( J_1 - J_2 - K \) model are still under debate. Long range nematic order is clearly not re-
required in \( \text{XFe}_2\text{As}_2 \), since the spin excitation spectrum at least at higher energies is little changed at temperatures well above the tetragonal-orthorhombic structure transition \[13\] \[17\] \[38\] \[39\]. The spin waves of \( \text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_2 \) could be described by either model. In particular the rhombic iron vacancy order which has already broken the \( C_4 \) symmetry forms at a temperature higher than 718 K \[21\]. The anisotropic \( J_{1a} \) and \( J_{1b} \) in \( \text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_2 \) could originate from the structural orthorhombicity and the possible orbital ordering \[20\]. For the \( J_1 - J_2 - K \) model, the exchange couplings are estimated to be \( J_1S = (J_{1a} + J_{1b})/2 = 11 \pm 3 \), \( J_2S = 17 \pm 2 \), and \( KS = (J_{1a} - J_{1b})/4 = 15.5 \pm 1.4 \text{ meV} \[30\]. The biquadratic term could be enhanced by the dynamic fluctuations in the chalcogen height. Distinguishing the two models microscopically is beyond the scope of this work.

We list in Table I the fitted magnetic exchange couplings and measured Fe spin values in a number of stripe materials. In spite of this, the exchange couplings measured in units of \( SJ \) are remarkably universal. This result is both striking and mysterious. It remains to be seen how this relates to the superconductivity in the doped materials.

In summary, we have studied the spin waves of the pure stripe AF order in \( \text{Rb}_{0.8}\text{Fe}_{1.5}\text{S}_2 \) over a wide range in reciprocal space and energy. Our inelastic neutron scattering data reveal that even though the stripe AF order has strikingly similar \( SJ \) with all the other iron pnictides and chalcogenides, it is almost an ideal \( S = 2 \) Heisenberg antiferromagnet with fully localized moments inducing Mott insulator behavior.

We thank Qimiao Si and Yao Shen for useful discussions. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC02-05CH11231 and the Office of Basic Energy Sciences U.S. DOE Grant No. DE-AC03-76SF008. We also acknowledge support from NBRPC-2012CB821400 and NSFC-11275279.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( S_{J_{1a}} )</th>
<th>( S_{J_{1b}} )</th>
<th>( S_{J_2} ) (meV)</th>
<th>( S )</th>
<th>( M(\mu_B) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaFe}_2\text{As}_2 )</td>
<td>50 ± 10</td>
<td>-6 ± 5</td>
<td>19 ± 4</td>
<td>1/2</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{BaFe}_2\text{As}_2 )</td>
<td>59 ± 2</td>
<td>-9 ± 2</td>
<td>14 ± 1</td>
<td>1/2</td>
<td>0.87</td>
</tr>
<tr>
<td>( \text{SrFe}_2\text{As}_2(L) )</td>
<td>31 ± 1</td>
<td>-5 ± 5</td>
<td>23 ± 1</td>
<td>0.30</td>
<td>0.94</td>
</tr>
<tr>
<td>( \text{SrFe}_2\text{As}_2(H) )</td>
<td>39 ± 2</td>
<td>-5 ± 5</td>
<td>27 ± 1</td>
<td>0.69</td>
<td>0.94</td>
</tr>
<tr>
<td>( \text{K}<em>{0.8}\text{Fe}</em>{1.5}\text{Se}_2 )</td>
<td>38 ± 7</td>
<td>-11 ± 5</td>
<td>19 ± 2</td>
<td>-</td>
<td>2.8</td>
</tr>
<tr>
<td>( \text{Rb}<em>{0.8}\text{Fe}</em>{1.5}\text{S}_2 )</td>
<td>42 ± 5</td>
<td>-20 ± 2</td>
<td>17 ± 2</td>
<td>2</td>
<td>2.8 ± 0.5</td>
</tr>
</tbody>
</table>

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[27] T. G. Perring, et al., http://tobyfit.isis.rl.ac.uk
Supplementary: Spin Waves and Spatially Anisotropic Electron Interactions in the $S = 2$ Stripe Antiferromagnet Rb$_{0.8}$Fe$_{1.5}$S$_2$

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FIG. S1: (color online). (a) Schematic of the iron layer with the rhombic iron vacancy order of the first twin, and (b) a simulation of the corresponding spin waves at $E = 30$ meV in the $[H,K]$ plane and (c) a simulation of the dispersion along the $[H,0]$ direction with the best fit parameters. The damping has been fixed at 3 meV for good viewability. The red arrow in (b) indicates the $Q$ in (c). (d) Schematic of the iron layer of the second twin. (e, f) The same plots with (b) and (c) for the second twin, respectively.

FIG. S2: (color online). The dispersion extracted from the experimental data of Rb$_{0.8}$Fe$_{1.5}$S$_2$ and the simulations with the parameters obtained from K$_{0.81}$Fe$_{1.58}$Se$_2$[28] along the (a) $[H,0]$ and (b) $[1,K]$ directions. The intensity of the simulations is proportional to $\chi''(q,\omega) \times \sqrt{E}$. 