Paramagnetic spin excitations in insulating Rb$_{0.8}$Fe$_{1.6}$Se$_2$

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(Received 8 October 2012; published 8 February 2013)

We use neutron scattering to study temperature-dependent spin excitations in insulating antiferromagnetic (AF) Rb$_{0.8}$Fe$_{1.6}$Se$_2$. In the low-temperature AF state, spin waves can be accurately described by a local moment Heisenberg Hamiltonian. On warming to around the Néel temperature of $T_N = 500$ K, low-energy ($E < 30$ meV) paramagnetic spin excitations form Lorentzian-like quasielastic peaks centered at the AF wave vectors associated with spin waves, while high-energy ($E > 50$ meV) spin excitations become heavily damped. Upon further warming to above the structural distortion temperature of $T_s = 524$ K, the entire paramagnetic excitations become overdamped. These results suggest that AF Rb$_{0.8}$Fe$_{1.6}$Se$_2$ is not a copper-oxide–like Mott insulator and has less electron correlations compared with metallic iron pnictides and iron chalcogenides.

DOI: 10.1103/PhysRevB.87.064409

PACS number(s): 75.30.Ds, 29.30.Hs, 75.50.Ee, 78.70.Nx

I. INTRODUCTION

Since the discovery of antiferromagnetic (AF) order in the parent compounds of iron pnictide superconductors,1,2 its microscopic origin and connection with superconductivity has been an issue of controversy.3 One class of models, rooted in the semimetallic nature of these materials,1 argues that the collinear AF order in the parent compounds such as BaFe$_2$As$_2$4 and SrFe$_2$As$_2$5 is the spin-density-wave type originating from the nesting of itinerant electrons between the hole and electron Fermi surfaces at $\Gamma$ and $M$ points in the Brillouin zone, respectively.6 On the other hand, there are reasons to believe that iron pnictides are not far away from a Mott insulator, where electron correlations are important in determining the transport and magnetic properties of these materials. The discovery of insulating $A_x$Fe$_{1.6+\delta}$Se$_2$ ($A = K$, Rb, Cs, Tl) near alkaline iron selenides superconductors8,9 provided a new opportunity to test whether the system is indeed a Mott insulator similar to the insulating copper oxides,10 an AF semiconductor,11 or an insulator with coexisting itinerant and localized electronic states controlled by the Hund’s rule coupling.12,13 Although the insulating $A_x$Fe$_{1.6+\delta}$Se$_2$ are isostructural with the metallic iron pnictides,3 they form a $\sqrt{5} \times \sqrt{5}$ block AF structure with a large ($\sim 3.3 \mu_B$ per Fe) $c$-axis aligned moment and iron vacancy order [Fig. 1(a)], completely different from the collinear AF structure of iron pnictides.14-16

Using time-of-flight neutron spectroscopy, we showed previously that spin waves in insulating Rb$_{0.8}Fe_{1.5}$Se$_2$ can be accurately described by a local moment Heisenberg Hamiltonian.17 For comparison, we note that there are still debates concerning whether a local moment Heisenberg Hamiltonian can appropriately model spin waves in iron pnictides.18-25 Moreover, recent spin wave measurements on iron chalcogenide Fe$_{1.1}$Te, which has a bicolinear AF structure and Néel temperature of $T_N = 67$ K,26-29 suggest that the effective spin per Fe changes from $S \approx 1$ in the AF state to $S \approx 3/2$ in the paramagnetic state, much different from the expectation of a conventional Heisenberg antiferromagnet.30 On the other hand, temperature-dependent paramagnetic scattering measurements in metallic AF BaFe$_2$As$_2$ reveal that high-energy ($E > 100$ meV) spin waves and the effective spin per Fe are essentially unchanged for temperatures up to 2.1$T_N$.31 Given such diverse results in the parent compounds of iron-based superconductors, it is important to study the evolution of spin waves in a well-defined local moment Heisenberg system expected to be close to a Mott transition.10

In this article, we report inelastic neutron scattering studies of paramagnetic spin excitations in AF Rb$_{0.8}$Fe$_{1.6}$Se$_2$. In the low-temperature insulating state, Rb$_{0.8}$Fe$_{1.6}$Se$_2$ forms a $\sqrt{5} \times \sqrt{5}$ block AF structure with a large iron ordered moment and iron vacancy order [Fig. 1(a)].14-16 Spin waves have three branches: one low-energy ($E \leq 30$ meV) acoustic spin wave branch stemming from the block AF ordering wave vectors, and two optical branches (at $E \approx 100$ and 200 meV, respectively) centered at wave vectors associated with spin waves in iron pnictides [Fig. 1(b)].31 and can be well described by a local moment Heisenberg Hamiltonian.17 On warming to 508 K above $T_N = 500$ K, the static AF order disappears but the lattice distortion induced by the iron vacancy order persists [Fig. 1(c)]. Here, paramagnetic spin excitations at low energies ($E \leq 30$ meV) form Lorentzian-like quasielastic peaks centered at the block AF wave vectors, whereas paramagnetic spin excitations at energies near optical spin waves are damped out [Fig. 1(d)]. Upon further warming to $T = 1.05T_s = 1.11T_N = 553$ K, the $\sqrt{5} \times \sqrt{5}$ iron vacancy induced lattice distortion vanishes and the system becomes tetragonal with disordered iron vacancies.16 The low-energy (<30 meV) paramagnetic spin excitations are only weakly correlated at the AF ordering wave vectors for iron pnictides. Therefore, the temperature dependence of spin waves in insulating Rb$_{0.8}Fe_{1.5}$Se$_2$ behaves like a local moment Heisenberg antiferromagnet, much different from that of metallic Fe$_{1.1}$Te30 and BaFe$_2$As$_2$.31 These results indicate that insulating Rb$_{0.8}$Fe$_{1.6}$Se$_2$ has less electron correlations and is not a copper-oxide–like Mott insulator.
II. RESULTS AND DISCUSSION

Our experiments were carried out at the MAPS time-of-flight inelastic neutron scattering spectrometer at ISIS, Rutherford-Appleton Laboratory, UK as described previously.21 We grew single crystals of Rb\textsubscript{0.8}Fe\textsubscript{1.6}Se\textsubscript{2} by normalizing the magnetic scattering to a vanadium standard (with 20\% error) throughout the paper. Compared with earlier spin wave work on ARCS at the Spallation Neutron Source, Oak Ridge National Laboratory,\textsuperscript{17} which has an error of 50\%, the present measurements were determined from inductively coupled plasma analysis with 1\% uncertainty.\textsuperscript{17}

The chemical composition of these samples was determined from inductively coupled plasma analysis and found to be slightly different from those of previous work.\textsuperscript{17} Below $T_N \approx 500$ K, Rb\textsubscript{0.8}Fe\textsubscript{1.6}Se\textsubscript{2} forms an Fe\textsubscript{4} block AF checkerboard structure with a $\sqrt{2} \times \sqrt{2}$ superlattice unit cell as shown in the shaded area of Fig. 1(a). We define the wave vector $Q$ at $(q_x, q_y, q_z)$ as $(H_0, K_0, L_0) = (q_x a_x/2\pi; q_y a_y/2\pi; q_z c_z/2\pi)$ reciprocal lattice units (rlu), where $a_x = 5.65$ Å and $c_z = 14.46$ Å are the orthorhombic cell lattice parameters (green shaded area), for easy comparison with spin waves in BaFe\textsubscript{2}As\textsubscript{2}.\textsuperscript{21,31} Considering both left and right chiralities from the AF order, there are eight Bragg peaks at wave vectors $(H_0, K_0, L_0)$ from the block AF structure, where $m, n = \pm 2, \pm 4, \ldots$, and $L_0 = \pm 1, \pm 3, \ldots$ [Fig. 1(b)]. We coaligned ~5 grams of single crystals of Rb\textsubscript{0.8}Fe\textsubscript{1.6}Se\textsubscript{2} (with mosaic <3°) and loaded them inside a high-temperature furnace. The temperature-dependent AF Bragg peak and superlattice reflection associated with the $\sqrt{2} \times \sqrt{2}$ iron vacancy order disappear at $T_N = 500$ K and $T_N = 524$ K, respectively [Fig. 1(e)]. This indicates the vanishing magnetic and structure orders consistent with earlier results on other A\textsubscript{6}Fe\textsubscript{6+}Se\textsubscript{2}.\textsuperscript{14–16} Figure 1(e) shows the evolution of the acoustic spin waves with increasing temperature along the dashed line of Fig. 1(b). At 300 K, there are well-defined spin waves stemming from the block AF ordered wave vectors [upper panel, Fig. 1(e)]. Upon warming up to $T = 1.02 T_N = 508$ K, paramagnetic spin excitations become much less well defined but still appear at the AF ordered wave vectors [middle panel, Fig. 1(e)]. Finally, on warming up to $T = 1.06 T_N = 553$ K, paramagnetic spin excitations become featureless with no evidence for spin correlations at the AF ordering wave vectors [bottom panel, Fig. 1(e)].

Figure 2 summarizes wave vector and temperature dependence of the low-energy acoustic spin excitations in the $[H_0, K_0]$ plane from 300 to 553 K. At $T = 0.6 T_N = 300$ K, spin waves are similar to the earlier results at 10 K,\textsuperscript{17} having a spin anisotropy gap at $E = 6 \pm 1$ meV and dispersing outward with increasing energy [Figs. 2(a), 2(d), 2(g), 2(j), and 2(m)]. In the AF ordered state, spin waves stem from the $\sqrt{2} \times \sqrt{2}$ in-plane wave vectors and $c$-axis wave vectors of $L = 1, 3, 5, \ldots$ On warming to $T = 1.02 T_N$, paramagnetic spin excitations become quasi-two-dimensional with no $c$-axis modulations. The spin anisotropy gap disappears and paramagnetic spin excitations move away from the $\sqrt{2} \times \sqrt{2}$ AF ordering positions for energies above $E = 30$ meV [Figs. 2(b), 2(e), 2(h), 2(k), and 2(n)]. Upon further warming to above 1K, paramagnetic spin excitations become very broad in momentum space and move to the AF wave vector of BaFe\textsubscript{2}As\textsubscript{2} instead of the block AF structure [Figs. 2(c), 2(f), 2(i), 2(l), and 2(o)].

Figure 3 shows the temperature dependence of the optical spin excitations. For the low-energy optical spin excitations at $E = 85 \pm 10$ meV, warming from 300 K [Fig. 3(a)] to 508 K [Fig. 3(b)] and 553 K [Fig. 3(c)] reduces the magnetic...
scattering intensity. This can be seen from the broadening of spin waves centered near the $(\pm 1,0)\,(0, \pm 1)$ positions at 300 K to paramagnetic scattering essentially all wave vectors at 553 K. At $E = 110 \pm 10$ meV, well-defined spin waves at 300 K [Fig. 3(d)] completely disappear at 508 K [Fig. 3(e)] and 553 K [Fig. 3(f)]. At $E = 165 \pm 15$ meV, there is no observable magnetic scattering at 300 K [Fig. 3(g)], 508 K [Fig. 3(h)], and 553 K [Fig. 3(i)]. Finally, spin waves centered near $(\pm 1, \pm 1)$ positions at $E = 195 \pm 15$ meV also vanish on warming from 300 K [Fig. 3(j)] to 508 K [Fig. 3(k)] and 553 K [Fig. 3(l)].

Based on data in Figs. 2 and 3, we construct in Figs. 1(b), 1(d), and 1(f) the evolution of spin waves to paramagnetic spin excitations in insulating Rb$_{0.8}$Fe$_{1.8}$Se$_2$. Comparing the result with dispersions of paramagnetic excitations in BaFe$_2$As$_2$, where high-energy spin excitations near the zone boundary are weakly temperature dependent for temperatures up to $2.1T_N$, we see that paramagnetic scattering in Rb$_{0.8}$Fe$_{1.8}$Se$_2$ behaves much like a conventional local moment Heisenberg antiferromagnet, forming Lorentzian-like quasielastic peaks centered at $E = 0$. To quantitatively determine the integrated magnetic moments and compare the outcome with those in Fe$_{1.1}$Te$_{0.9}$ and BaFe$_2$As$_2$, we plot in Fig. 4 the temperature dependence of the local dynamic susceptibility for Rb$_{0.8}$Fe$_{1.8}$Se$_2$. For a local moment system with spin $S$, the total moment sum rule requires $M_0 = (g \mu_B) S (S + 1)$ when magnetic scattering is integrated over all energies and wave vectors. For iron in the 3$d^6$ electronic state, the maximum possible moment is $gS = 4 \mu_B$ and $g = 2$, thus giving $M_0 = 24 \mu_B^2/Fe$. In previous work, we estimated that the total moment sum rule is exhausted for Rb$_{0.8}$Fe$_{1.8}$Se$_2$ below $\sim 250$ meV. The energy dependence of the local susceptibility becomes progressively weaker on warming from 300 to 508 and 553 K [Fig. 4(a)]. Figure 4(b) shows temperature dependence of the ordered moment (open diamonds)
investigated (solid circles). Consistent with earlier results, 17
we find that the total moment sum rule is almost exhausted
for Rb$_{0.8}$Fe$_{1.6}$Se$_2$ at 300 K, corresponding to a full moment
of $gS = 4 \mu_B$/Fe with $S = 2$. On warming to 508 and 553 K, the
total integrated moment drops dramatically, reflecting the fact
that our unpolarized neutron scattering experiment can only probe
correlated magnetic excitations and is not sensitive to
wave-vector–independent paramagnetic scattering. For compari-
son, we note that the integrated magnetic spectral weight of
Fe$_{1.1}$Te was found to increase from the AF state to the
paramagnetic state. 30 While the total integrated moment of
BaFe$_2$As$_2$ remains essentially unchanged from $T_N = 500$ K,
we find that the total moment sum rule is almost exhausted
for Fe$_{1.1}$Te. 30 To illustrate this point, we plot in Fig. 4(c)
the normalized total fluctuating moment $|M(T)/M(T_{\text{min}},K)|$
where $M(T_{\text{min}},K)$ is integrated local moment in the lowest
temperature of the AF ordered state as a function of $T/T_N$
for Fe$_{1.1}$Te, 30 BaFe$_2$As$_2$, 31 and Rb$_{0.8}$Fe$_{1.6}$Se$_2$. It is clear that
the temperature dependence of the fluctuating moment in
Rb$_{0.8}$Fe$_{1.6}$Se$_2$ behaves differently from the other iron-based
materials.

Comparing with iron pnictide BaFe$_2$As$_2$ and iron chalcogenide
Fe$_{1.1}$Te, insulating Rb$_{0.8}$Fe$_{1.6}$Se$_2$ appears to be a
classic local moment Heisenberg antiferromagnet. The lack of
correlated high-energy paramagnetic spin excitations in
Rb$_{0.8}$Fe$_{1.6}$Se$_2$ suggests that electron correlation effects are
smaller in Rb$_{0.8}$Fe$_{1.6}$Se$_2$, contrasting with iron pnictides 31 and
iron chalcogenide. 30 This is also different from prototypical
Mott insulators such as parent compounds of copper-oxide
superconductors, where paramagnetic spin excitations above
100 meV are not expected to be different from spin waves
below $T_N$. 35 Our data thus suggest that insulating $A_x$Fe$_{1.6+x}$Se$_2$
is not a copper-oxide–like Mott insulator. Alternatively, if
insulating $A_x$Fe$_{1.6+x}$Se$_2$ is a semiconductor with an energy gap
of $\sim 500$ meV opened below the $\sqrt{5} \times \sqrt{5}$ AF but not below
the iron vacancy ordering temperature, 11 one would expect
spin excitations to change dramatically from below to above
$T_N$ but not significantly across $T_s$. Although paramagnetic spin
excitations in the iron vacancy ordered state ($T = 508$ K) do
appear at the $\sqrt{5} \times \sqrt{5}$ AF wave vectors for $E < 20$ meV
(Figs. 2(b), 2(e)), higher energy acoustic and optical spin ex-
citations are heavily damped and are sensitive to the magnetic
but not to the iron vacancy order (Figs. 2 and 3). This is
consistent with the idea that insulating Rb$_{0.8}$Fe$_{1.6}$Se$_2$ is an AF
semiconductor. 11 Finally, if magnetism in Rb$_{0.8}$Fe$_{1.6}$Se$_2$ arises
from a combination of itinerant electrons and local moments
due to Hund’s rule coupling similar to other iron-based
materials, 32,13,36 its paramagnetic spin excitations should behave similarly as well. Since paramagnetic spin excitations in
iron chalcogenide and pnictides 30,31 are clearly different from those of Rb$_{0.8}$Fe$_{1.6}$Se$_2$ [Fig. 4(c)], our data adds to the debate on why superconductivity in $A_x$Fe$_{1.6+x}$Se$_2$ always
appears near the $\sqrt{5} \times \sqrt{5}$ AF insulating phase 14–16 and
which material is the true parent compound of $A_x$Fe$_{1.6+x}$Se$_2$
superconductors. 37,38

III. SUMMARY AND CONCLUSIONS

We have used neutron scattering to study temperature-
dependent spin excitations in insulating antiferromagnetic
(AF) Rb$_{0.8}$Fe$_{1.6}$Se$_2$. At low temperature, the system forms a
$\sqrt{5} \times \sqrt{5}$ block AF structure with a large iron ordered moment
along the $c$ axis and iron vacancy order. As a function of
increasing temperature, Rb$_{0.8}$Fe$_{1.6}$Se$_2$ first changes into a para-
magnet around the Néel temperature of $T_N = 500$ K but still
maintains a $\sqrt{5} \times \sqrt{5}$ iron vacancy order. Upon further warm-
ing to $T_s = 524$ K, the iron vacancy order disappears. Our time-
of-flight inelastic neutron scattering experiments reveal that
the low-energy ($E < 30$ meV) paramagnetic spin excitations
form Lorentzian–like quasielastic peaks centered at the AF
wave vectors associated with spin waves, while high-energy
($E > 50$ meV) spin excitations become heavily damped
around 500 K. Upon further warming to above $T_s = 524$ K, the
entire paramagnetic excitations become overdamped. By
comparing these results in absolute units with previous work
on temperature-dependent spin excitations in AF iron pnictide
BaFe$_2$As$_2$ 31 and iron chalcogenide Fe$_{1.1}$Te, 30 we conclude that
AF Rb$_{0.8}$Fe$_{1.6}$Se$_2$ is not a copper-oxide–like Mott insulator and
has less electron correlations compared with metallic iron pninc-
tides and iron chalcogenides. Its spin excitations in the param-
agetic state are consistent with a prototypical local moment
antiferromagnet.

ACKNOWLEDGMENTS

We thank Tao Xiang, J. P. Hu, and Guangming Zhang
for helpful discussions. The work at UTK is supported by
the US DOE BES No. DE-FG02-05ER46202. Work at the
IOP, CAS is supported by the MOST of China 973 programs
(2012CB821400, 2011CBA00110) and NSFC-51002180.
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